AN OUTLINE
OF
WAVE MECHANICS

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AN OUTLINE
OF
WAVE MECHANICS

by

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INTRODUCTION

This book is based on a course of lectures which I gave in the Physics Department of the University of Manchester in the winter of 1929–30. I would like to thank many members of the staff for their suggestive criticisms.

It has been my aim to give an account of the methods of the New Quantum Theory that should be intelligible to the advanced student of experimental physics, and to the research worker. It is assumed that the reader is familiar with the outstanding successes and difficulties of the Old Quantum Theory, as they stood in 1923. An acquaintance with Fourier analysis is also required, and with the elementary principles of wave motion. No use is made, either of the Principle of Least Action, or of the Theory of Relativity.

I would like to thank both Mr R. W. James and Mr P. M. S. Blackett, who read the book in manuscript and made several suggestions for its improvement.

N. F. MOTT

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CONTENTS

CHAP.		PAGE
I.	Waves and Particles	1
II.	The Wave Equation	27
III.	Group Velocity and the Uncertainty Principle	39
IV.	The Theory of Stationary States	55
V.	The Absorption of Radiation	82
VI.	The Helium Atom and the Hydrogen Molecule	91
VII.	Dynamics of Systems containing many Electrons	119
VIII.	The Spin of the Electron and the Exclusion Principle	135
Appendix		151
Index		157

CHAPTER I

WAVES AND PARTICLES

SECTION I

The Quantum Theory, originated by Planck and developed by Bohr and his school, accounted successfully for a large class of those phenomena that the older theories could not explain. Among these were the photoelectric effect, the X-ray absorption spectra, and the optical spectra of the simpler atoms. On the other hand, the theory could not be reconciled with the wave nature of light. The basic postulate of the quantum theory, a postulate amply proved by experiment, is that light of frequency ν can only give up its energy in quanta, of energy $h\nu$. No other waves known to physics behave in this way, and yet the wave theory of light is founded on evidence too conclusive to admit of any doubt.

The new theory of matter that we call the wave mechanics, developed in the last five years by Heisenberg, Schrödinger, Dirac and others, owes its inception to an attempt to include the quantum and wave properties of light within a single scheme. It has been eminently successful. The theory has been able to account for all the phenomena that either Newtonian mechanics or the old Quantum Theory could explain, and for a large number that resisted both of them. The wave- and quantum-like properties of light both have their place in the theory, but they no longer appear in contradiction to one another.

In order to understand the way in which the new theory effects this reconciliation, it is necessary to examine the evidence upon which the wave theory of light is based. Light manifests itself primarily as a flow of energy; the energy affects the retina of the eye, or blackens a photographic plate. A theory of light should tell us, among other things, how this energy is propagated through space. There are two ways known to physics in which

energy can flow from place to place: either as the kinetic energy of a stream of moving particles, or as the energy of a wave train in some medium. The wave theory is based on the assumption that the transference of energy is effected in the second of these two ways. This assumption is made in order to account for the phenomenon of interference; we have no direct knowledge of a medium that actually oscillates, in the same sense that the water oscillates in a water wave, or as the air molecules oscillate in a sound wave. In the early days of the wave theory, however, it was assumed that there was a medium of some kind, for waves

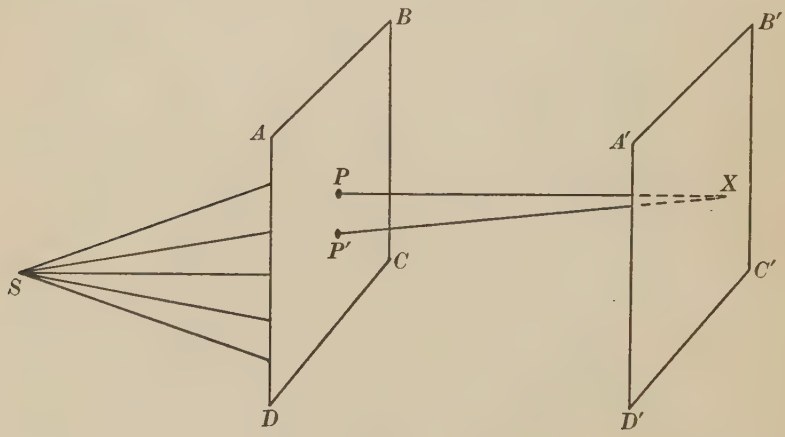


Fig. 1.

could not be thought of as existing otherwise than in a medium; and further, since energy is transferred by a light wave, it was assumed that the medium possessed inertia. This medium was called the aether.

Let us now consider the simplest possible interference experiment. Let S (Fig. 1) be a source of monochromatic light, and $A'B'C'D'$ a screen, perhaps a photographic plate. An opaque screen $ABCD$ is put between S and $A'B'C'D'$, in which are two pinholes close together, P and P'. Energy in the form of light is being transferred from the source S to the screen $A'B'C'D'$. It is found

that the rate at which the screen receives energy is not uniform for all points X of the screen, but is zero if

$$PX - P'X = \tfrac{1}{2}(2n + 1)\lambda \qquad \ldots\ldots(1),$$

whereas at points for which

$$PX - P'X = n\lambda \qquad \ldots\ldots(2),$$

the screen receives four times as much energy as it would receive from either pin-hole, were the other one covered up. n in these formulae is zero, or any whole number; λ is a length depending on the colour of the light. We call λ the wave length of the light; but it is experiments such as the one described that give physical meaning to the idea of wave length. It is clear how beautifully the interference fringes are accounted for if a beam of monochromatic light is assumed to consist of a train of waves of just this wave length λ; for in a train of waves in any medium the rate of transfer of energy is proportional to the square of the amplitude of the wave. Therefore, at any point X satisfying (1), where the waves from P, P' have opposite phase, the resultant amplitude is zero, and no energy is transferred to the screen; whereas at points satisfying (2), where the two waves are in phase, the resultant amplitude is twice that produced by a single wave, and the rate of energy transfer is four times greater. It is clear that if the energy were transferred from P, P' to the screen as the kinetic energy of a stream of moving particles, no such interference effect could possibly occur.

There is no direct way of measuring the frequency of these waves, or their wave velocity. The experiments on the velocity of light reveal only the group velocity c, which is found to be independent of the wave length. It is consistent with all the known facts to assume that the wave velocity is also equal to c, though this cannot strictly be deduced from our knowledge of the group velocity. The frequency will then be equal to c/λ. In speaking of the frequency of a light wave, we shall mean simply c divided by the wave length.

During the last thirty years, it has become more and more evident that light has many properties that cannot be reconciled

with the wave theory. The most striking of these is the photoelectric effect. If X-rays fall on the atoms of, say, a gas, electrons are emitted. These are called "photoelectrons." If the X-rays are monochromatic, all the electrons are ejected with the same energy. This energy does not depend on the intensity of the X-rays, but only on their frequency. With diminishing intensity we obtain merely fewer photoelectrons. If E be the energy with which a photoelectron is ejected, then

$$E = h\nu - P.$$

P is a constant for a given type of atom, and must represent the amount of energy required to remove an electron from the atom; ν is the frequency of the X-rays; h is Planck's constant. It appears, therefore, that when X-radiation gives up energy to matter, the energy is not transferred continuously but in little "quanta" of amount $h\nu$. This is just what would happen if the energy of light moved from place to place as the kinetic energy of small particles, which could give up their energy to matter when they came in contact with it. It is difficult to see how a wave could give up its energy otherwise than continuously.

It was to explain the photoelectric effect that Einstein, passing over the phenomenon of interference, brought forward his theory of light quanta. He assumed that the energy in a beam of light was carried by a stream of moving particles, each moving with velocity c and having kinetic energy $h\nu$. The "rest mass" of each particle must be zero*, for otherwise, according to the relativity theory, its energy would be infinite. This fact would account for the disappearance of a light quantum when it has given up its energy, for a particle with neither mass nor charge nor energy could hardly be observable. A monochromatic beam of light in which energy A^2c crosses unit area in unit time will be represented by a beam containing $A^2/h\nu$ light quanta per unit volume, instead of by a wave of amplitude equal to A. The momentum of each particle will be $h\nu/c$, so the theory gives a correct description of the rate of flow of momentum, as well as

* Cf. Appendix, Note 1.

accounting for the photoelectric effect. It is, of course, completely at variance with the facts of interference.

Further striking evidence in favour of the light quantum hypothesis was afforded by the discovery of the Compton effect. If light falls on a free electron, we should expect, according to the wave theory, that the electron would vibrate under the influence of the waves, and that the vibrating electron would give out light of the same frequency as that of the original light. Now it is difficult to carry out experiments on free electrons; but the electrons bound in an atom behave as though they were free when under the influence of light of very short wave length, that is to say, of hard X-rays. Actually, it is found that when X-rays fall on an atom, some of the scattered radiation has lower frequency, and also that electrons are ejected from the atom. Some of these are the photoelectrons already referred to, but some have less energy. The whole phenomenon can be accounted for quantitatively by the assumption that light consists of particles, or quanta, of momentum $h\nu/c$, which collide with electrons and are deflected by them, momentum being conserved at the collision*.

These two examples are typical of a host of experiments which show that the energy of light is not found distributed uniformly through space as it would be in a wave, but localised in little bundles. Whenever light gives up its energy to matter, it does so in a way that can be accounted for by the light-quantum hypothesis. (Light, of course, can only be "observed" by the energy it gives to matter.) The wave theory is still needed to explain the way in which light is propagated through space, and the way in which beams reinforce one another. It is the first task of the new mechanics to fit these two theories into a consistent whole.

It can scarcely be said that the contradiction between the two theories has at the present day been solved; what has been done is to develop rules which tell us just *when* light behaves as particles and *when* as waves. These rules do not enable us to

* For a full account, see Andrade, *The Structure of the Atom*, 3rd ed., p. 688.

form any picture in our minds of how the particles move; but they enable us to predict what we shall observe in any experiment. A physical theory can do two things: it can enable us to form a picture in our minds of what is happening, and to predict the results of experiments. The present theory certainly only does the latter. But let us turn to a definite experiment and see what these rules must be.

The conflict between the wave and particle ideas, and the way in which the new mechanics deals with it, is well illustrated by the simple interference experiment that we have described. If the light were of sufficiently high frequency, photoelectrons would be emitted from the screen $A'B'C'D'$. Many more would come from the points where (2) is true than from the points near (1). The wave- and particle-like properties are in evidence in this experiment at the same time. In order to describe what happens, and to bring both properties within the same scheme, we make the following somewhat strange assumptions about the nature of light. We shall suppose that the light *waves* have of themselves no energy. The energy is carried by particles which we shall call light quanta. And instead of assuming that, if A is the amplitude of the light waves, A^2 is the mean energy density in the aether, we shall assume that $A^2/h\nu$ is the mean number of light quanta in the volume element $d\tau$. Statistically the assumptions give the same energy density; if we take a volume large enough to include many light quanta, then, since the energy of each particle is $h\nu$, the energy inside the volume is $\int A^2 d\tau$. But whatever vibrates in the wave is not now a strain in a real medium possessing energy, but simply a mathematical function which enables us to predict what the density of light quanta will be.

The method is quite general. If a beam of monochromatic light passes through any series of slits or refracting media, we can calculate its path by means of the classical wave theory of light. However, when the light comes to give up energy to matter, it does so in quanta of amount $h\nu$. The rate at which

these quanta are given up can be calculated by assuming that the number of light quanta per unit volume is $A^2/h\nu$. The number of light quanta that will be given up in time T on an area dS of an absorbing screen placed perpendicular to the motion of the light is then $A^2.cT.dS/h\nu$.

We do not claim, in making these assumptions, to have given any explanation of the dual nature of light. We have merely fitted the observed facts into a mathematical scheme. We cannot state what paths are followed by the light quanta. We should be very dissatisfied with our theory were it not for the recent discovery that electrons, as well as light quanta, have this dual nature. This discovery is at the basis of the wave mechanics.

If a beam of X-rays strikes a crystal surface, it is reflected only for certain definite angles of incidence. These angles depend on the wave length of the X-rays used, and on the spacing of the atoms in the crystal. At these angles the waves reflected from the successive layers of atoms are in phase and reinforce each other; at all other angles they are out of phase and interfere destructively*. Now if a beam of electrons strikes a crystal surface, exactly the same thing happens; the beam is only scattered for a few special angles of incidence†. These angles depend on the spacing, as before, and on the velocity of the electrons. The conclusion is inevitable that a beam of electrons behaves in some ways like a beam of waves, and that the wave length of the waves depends on the velocity of the electrons. Further, when we have measured the angles for which the beam is reflected, and if we know the spacing in the crystal, we can calculate the wave length of these waves in just the same way as is done for X-rays. The wave length turns out to be h/mv, where m is the mass of an electron, h is Planck's constant, and v is the velocity of the electrons in the beam.

* For a full discussion, see W. H. and W. L. Bragg, *X-rays and Crystal Structure*, Chap. II.

† This effect was first found by Davisson and Kunsman in 1923. Cf. *Phys. Rev.* vol. XXII, p. 242, 1923; these experiments were uncertain. The effect was definitely established by Davisson and Germer, cf. *Phys. Rev.* vol. XXX, p. 705, 1927.

Electrons, then, just like light, behave sometimes as waves and sometimes as particles. We can fit their two properties into one scheme in very much the same way as we did for light. We make the following assumptions about the nature of electrons. Electrons are particles; that is to say, their charge and mass and energy are always observed in particle form, not spread about continuously in space. But if we want to calculate the path of a beam of electrons, and whether and how it is reflected by a crystal, we must treat the beam as though it were a beam of waves. These waves we call "de Broglie" waves. We assume that they are propagated through space, reflected and refracted in much the same way as light waves. This we shall discuss in the next section. And if we want to know how many electrons there are anywhere we must follow much the same procedure as for light quanta. If B be the amplitude of the de Broglie wave at any point, we assume that the density of electrons at that point is proportional to B^2.

Since these waves are not observable except through the property that more electrons are found where the amplitude is greatest, the unit in which we measure this amplitude is at our choice. It is convenient to choose it in such a way that the density of electrons at any point is *equal* to B^2. The number of electrons in any volume is then $\int B^2 d\tau$, the integral being taken over the volume. The flow across unit area per unit time is $B^2 v$.

Again, these assumptions provide no model of the way in which electrons move; we have merely given a mathematical description of the observed facts. But de Broglie waves have certainly as much physical reality as light waves, and light quanta as electrons. In both cases we observe particles, and in both cases, if we want to know where the particles are, we must assume the presence of waves, and derive the *density* of particles at any point from the square of the amplitude of these waves.

We have spoken of the density of the particles; it must not be thought that de Broglie waves can only be used to describe

beams of such density that a region in which the amplitude is constant will contain a great many electrons. If a beam of electrons were to fall on a crystal it would only be reflected for certain angles of incidence, even though the beam were so weak that only one electron fell per minute. To describe such a beam, we shall assume that $B^2 d\tau$ is the *probability* that an electron is in the volume element $d\tau$ at any moment. Thus, if the wave flows across a surface for a *long* time T, then the number of electrons passing the surface element dS is $vB^2T\,dS$.

There is no property of streams of electrons that is at all similar to the polarisation of light waves. Until the last chapter, in which we consider the spin of the electron, we shall treat these waves as scalar waves. Many of their properties are more similar to those of sound waves, which consist of a periodic variation of a scalar quantity, the pressure, than to those of vector waves such as light.

SECTION II

REFRACTION

If we knew how an electron behaved in an electromagnetic field, we should be able to account for a great many of the facts of physics. A hydrogen atom is nothing more than an electron moving in an inverse square law electrostatic field, and therefore we should be able to predict its energy levels. The scattering of beams of electrons, whether by free atoms or by the atoms of a crystal, could also be accounted for numerically.

Now we have postulated, in order to account for the experimental results of Davisson and Germer and others on the diffraction of beams of cathode rays, that the behaviour of a beam of electrons is similar to the behaviour of a beam of waves of wave length h/mv. If our assumption is correct, it ought to be possible to show theoretically that these beams of waves do behave in electric fields in the same way as beams of electrons are actually observed to do.

In this chapter we shall confine ourselves to electrostatic

fields. These may be either the comparatively weak fields obtainable in the laboratory, or the very strong fields that must exist inside an atom. It is in describing the effect of the latter that the old Newtonian mechanics went wrong, and quantum ideas had to be introduced. But beams of electrons entering ordinary laboratory electrostatic fields are found to be bent in exactly the same way as the Newtonian mechanics say that they ought to be. Therefore we ought to be able to show that a beam of waves, with the wave length that we know these waves to have, is bent by the field in just this way. If this were not so, the theory would give an incorrect account of the facts and we should have to abandon it.

However, we can easily see that the waves are bent in just this way. When an electron enters an electric field its velocity changes. The beam of electrons, we assume, will behave like a beam of waves. The wave length of the waves depends on the velocity of the electrons that they represent. Therefore, the wave length of waves, in the field, will be different from the wave length in free space. The field, therefore, acts on these waves in just the same way as a refracting medium acts on, let us say, light waves; it simply alters the wave length. Further, we can easily see how much it alters the wave length, and so obtain the refractive index. Let E be the energy of each electron, and V (xyz) the potential energy that it would have at any point (xyz) in the electric field. Then the velocity of the electron at that point will be $\sqrt{2\,(E-V)/m}$. Therefore the wave length of our waves at the point (xyz) will be $h/\sqrt{2m\,(E-V)}$. Since the wave length in "free space," i.e. where the field vanishes, is $h/\sqrt{2mE}$, the refractive index, equal to the ratio of these two, is $\sqrt{E/(E-V)}$, at the point (xyz). The refractive index, we see, depends on E, and therefore on the wave length of the waves in free space, just as it does also for light waves.

It is now a very simple matter to work out how these beams are bent by a field, the problem being the same as that of finding the path of a ray of light in a medium of varying refractive index. We shall give a discussion of the bending of any wave

beam in a refracting medium, and show that for de Broglie waves refracted by an electric field, the bending is just what the Newtonian mechanics would predict for a beam of electrons.

Fig. 2 represents part of the beam. We confine ourselves, for simplicity, to a medium that only varies in one plane, which we shall take to be the plane of the paper. Let PQ, $P'Q'$ be the intersection of two successive wave fronts with the plane of the

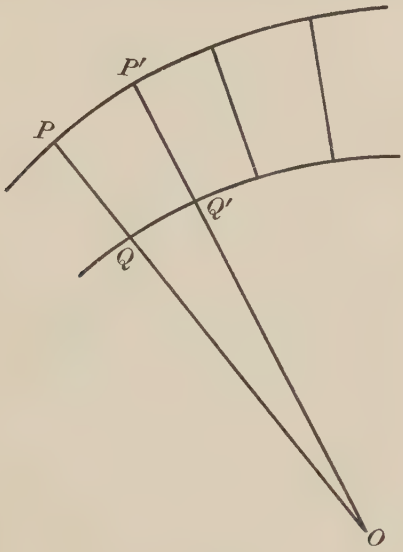


Fig. 2.

paper. Let PQ, $P'Q'$ intersect in O; then O is the centre of curvature of the path, as accurately as a broad thing like the path of the beam can be said to have a centre of curvature. In the same sense, OQ is equal to the radius of curvature. Let us denote this length by R. Let σ denote the breadth PQ of the beam, and $\frac{\partial}{\partial n}$ differentiation normal to the direction of motion of the waves; i.e. along QP. Let λ be the wave length in the neighbourhood of Q, Q'; then in the neighbourhood of P, P' the

wave length will be $\lambda + \frac{\partial \lambda}{\partial n}\sigma$. Now by definition PP' and QQ' are both wave lengths; therefore

$$QQ' = \lambda, \quad PP' = \lambda + \frac{\partial \lambda}{\partial n}\sigma.$$

Now from the similar triangles OQQ', OPP' we can find a relationship between λ, σ and R; for we have

$$OP : OQ = PP' : QQ',$$

i.e.
$$\frac{R+\sigma}{R} = \frac{\lambda + \frac{\partial \lambda}{\partial n}\sigma}{\lambda}.$$

Thence we obtain
$$\frac{1}{R} = \frac{\partial \lambda}{\partial n} \Big/ \lambda$$
$$= -\frac{1}{N}\frac{\partial N}{\partial n},$$

if N be the wave number*.

The radius of curvature at every point is therefore known, and so the path could be traced. If the waves are light waves of frequency ν, in a medium of varying refractive index μ, then the wave length is equal to $c/\mu\nu$, and therefore

$$\frac{1}{R} = -\frac{\partial}{\partial n}\log \mu,$$

a formula which is equivalent to Fermat's Principle of Least Time in Geometrical Optics. For our de Broglie waves,

$$N = \sqrt{2m\,(E - V)}/h.$$

Therefore
$$\frac{1}{R} = \frac{\partial V}{\partial n} \Big/ 2\,(E - V) \qquad \ldots\ldots(3).$$

This curvature, it is easily shown, is just the curvature that the beam would have if the electrons in it behaved according to the Newtonian mechanics. For, according to the Newtonian mechanics, a particle must move in such a way that the centrifugal force just balances the external force acting upon it. The centrifugal force in the direction QP is equal to mv^2/R, R being

* Throughout this book we shall use the term "wave number" to denote the reciprocal of the wave length.

the radius of curvature of the path at the point considered. The force, along PQ, due to the electrostatic field is $\frac{\partial V}{\partial n}$. Equating these two, we obtain

$$\frac{\partial V}{\partial n} = mv^2/R$$
$$= 2(E - V)/R.$$

Therefore the curvature is just that given by (3).

SECTION III

BOUNDARY CONDITIONS

Wave theory and particle theory, then, agree in the predictions that they make about the behaviour of beams in the ordinary weak electrostatic fields available in the laboratory. To obtain disagreement, we must consider strong fields, fields so strong that they change the velocity appreciably, and hence the wave length, in a distance comparable to the wave length itself. Such fields are only found within the atom.

The effect of such fields on our de Broglie waves will be somewhat similar to the effect of a medium of sharply varying refractive index on light waves. Now we cannot tell the effect of such a medium on the waves simply from a knowledge of the refractive index everywhere; for instance, if a beam of light falls on a slab of glass, at the face of which the refractive index changes suddenly from unity to about 1·5, we cannot tell how much of the energy of the beam is reflected, and how much goes through, unless we know what "boundary conditions" the wave has to satisfy at the face. Light waves, however, are not altogether suitable for the purpose of illustrating the behaviour of de Broglie waves, for the disturbance in a light wave is a vector, and in a de Broglie wave a scalar*. We shall therefore turn our attention to sound waves in a gas. These waves may be thought

* We do not wish to state definitely that these waves are scalar waves. The phenomenon of the spin of the electron suggests that they have some resemblance to vectors. We assert only that the phenomena discussed in the first seven chapters of this book can be treated without assigning to them vector properties.

of as periodic variations in the pressure, and therefore as scalar waves. Now the velocity of sound in a gas of given pressure depends on the density of the gas. Therefore, if two gases of different densities are separated by a light membrane that is free to move, then at the boundary between the two gases there is a sudden change in the wave velocity and therefore in the refractive index. If a plane wave falls on the membrane, then some of it will be reflected and some of it will be transmitted. To find out how much of the wave is reflected we must know the boundary conditions satisfied by the wave. One condition is clearly that p, the pressure, must be the same on both sides of the membrane. The other is that the actual motion of the gas shall be the same on both sides. Now, if ρ be the density of any gas, then the acceleration f of any volume element of the gas is given by

$$\rho f = \frac{\partial p}{\partial z}.$$

Since f must be continuous across the membrane, it follows that the boundary conditions, expressed in terms of p, are that

$$p, \quad \frac{1}{\rho}\frac{\partial p}{\partial z}$$

should be continuous at the boundary. If we draw a graph, therefore, plotting p against the distance in the direction of the wave train, the curve obtained would resemble that of Fig. 3. There would be a sharp "kink" in the curve at the boundary between the two media.

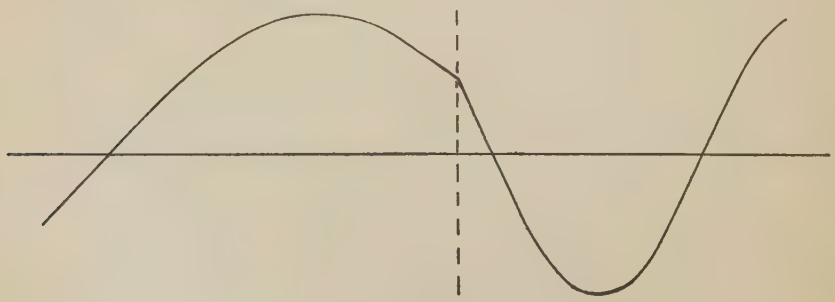


Fig. 3.

Using these boundary conditions we can find out how much of the wave is transmitted and how much reflected. Let N, N' be the wave numbers of the waves in the two gases. Then let us write for the wave in the first gas

$$p = e^{2\pi i\nu t}\,[e^{-2\pi iNz} + a e^{2\pi iNz}],$$

representing an incident wave of unit amplitude, and a reflected wave of amplitude a. In the second gas let the transmitted wave be

$$p = b e^{2\pi i\nu t} e^{-2\pi iN'z}.$$

Let us suppose that the plane $z = 0$ is the boundary between the two gases, and let ρ, ρ' be the densities of the two gases. Then, if we put in the boundary conditions found above, we obtain

$$1 + a = b, \qquad N\,(-\,1 + a)/\rho = -\,N'b/\rho'.$$

Hence we obtain

$$a = \frac{N - N'\kappa}{N + N'\kappa}, \quad b = \frac{2N}{N + N'\kappa} \qquad \ldots\ldots(4),$$

where

$$\kappa = \rho/\rho'.$$

Equation (4) gives the amplitudes of the reflected and transmitted waves.

Now suppose that a stream of electrons were to impinge on a "potential jump." By a "potential jump" we mean a repulsive electrostatic field that extends through a distance short compared to the wave length, but nevertheless so strong that it slows the electrons up appreciably, even in this short distance. After the electrons have passed the potential jump they are supposed to go on their way with uniform velocity. It is not suggested that anything of the sort exists in nature, but the idea is useful in discussing the behaviour of de Broglie waves. For the wave train of de Broglie waves, which we are assuming to behave in the way that real electrons do behave, will have different wave lengths on the two sides of the potential jump, and therefore the wave train as a whole ought to behave something like a train of light waves entering a refracting medium, such as a slab

of glass, or as a sound wave passing from one medium to another. Part of the beam will be reflected at the potential jump and part will go through. If then the wave mechanics do describe the way real beams of electrons behave, it follows that they behave in these circumstances quite differently from the way in which the Newtonian mechanics would lead one to expect. For the reflected beam must represent a stream of electrons reflected from the potential jump, and the transmitted wave a beam that goes through. According to the old theories, they will *all* get through (unless the potential jump is too high, in which case they will all be reflected). Unfortunately, it is impossible to test, by direct experiment, which theory is right, because it is impossible to make a field strong enough to slow up the electrons appreciably in a distance small compared to the wave length (10^{-8} cm.).

In order to find how much of the wave is reflected, we must know the boundary conditions that are to be satisfied at the two sides of the potential jump. Let, then, ψ be the "wave function," i.e. whatever it is that performs these oscillations, the square of whose amplitude determines the density of electrons in the beam. Now, we have no *a priori* knowledge of what the boundary conditions ought to be. We must merely guess them, and see if the beams so obtained fit the facts. We shall therefore make the assumption that ψ, like p in the sound wave just considered, must be continuous at the boundary. If ψ behaves at all similarly to the displacement in a wave in a material medium, then this must be the case.

Having made this assumption, we must find what condition $\frac{\partial \psi}{\partial n}$ satisfies. Suppose that the condition is that $\frac{\partial \psi}{\partial n}$ on one side of the boundary shall be equal to $\kappa \frac{\partial \psi}{\partial n}$ on the other, where κ is some constant depending on the potential jump. This, of course, is a pure assumption; but there must be a second boundary condition, to determine how much of the beam is reflected; and, by analogy with other kinds of wave motion, the condition is likely to be of this type.

We can deduce the value of κ. The result (4) obtained for sound is immediately applicable to de Broglie waves, writing ψ for p. In the incident wave there is one electron per unit volume. If v be the velocity of the electrons to the left of the potential jump, and v' be the velocity to the right, then the solution represents v electrons falling on the boundary per unit time per unit area, a^2v reflected, and b^2v' transmitted. Now the number of electrons transmitted, and the number reflected, must together be equal to the number that fall on the potential jump. We must have, therefore,

$$v = a^2v + b^2v'.$$

Putting in the values (4) of a and b, and remembering that $v : v'$ is equal to $N : N'$, we obtain

$$1 = \frac{(N - \kappa N')^2 + 4NN'}{(N + \kappa N')^2},$$

an equation whose only solution is

$$\kappa = 1.$$

The boundary conditions satisfied by the wave at a surface where V changes discontinuously are therefore that

$$\psi, \quad \frac{\partial \psi}{\partial n}$$

should be continuous. Therefore, if we plotted ψ against the distance along the wave, there would be no "kink" in the curve.

The boundary conditions satisfied by the wave are of great importance, because, together with our knowledge of the wave length at any point, they enable us to calculate the behaviour of a steady monochromatic wave in *any* field. This we shall show in the next chapter, when we discuss the wave equation satisfied by these waves. We can, however, work out, without the use of the wave equation, what happens to these waves if they fall on a small region of space, such as an atom, in which there is an electrostatic field. To see this, let us consider the behaviour of light waves, when they fall on a particle of refracting medium,

the dimensions of which are of the order of magnitude of the wave length. The waves are scattered. To calculate the scattering, it is assumed that each atom of the refracting medium scatters a wavelet. There are a large number of atoms in an element of volume small compared to the wave length, and so we may say that each element of volume $dxdydz$ of the medium scatters a wavelet of amplitude proportional to $dxdydz$. The amplitude of the scattered wavelet is also proportional to the extent that the atoms are polarised by the wave, and is therefore proportional to the amplitude of the incident wave at that point, if by amplitude is meant the maximum value of the electric force. The amplitude depends also on the number of atoms per unit volume, and on the polarisability of the atoms for light of the wave length considered. There is nothing else that it can depend on.

Now when de Broglie waves fall on an atom they are scattered. The law that governs the scattering is, as we shall show, that each element of volume $dxdydz$ scatters a wavelet, and that the amplitude of this wavelet, at distance R from the element of volume, is

$$\frac{2\pi m}{h^2} V(xyz).dxdydz/R \qquad \ldots\ldots(5)$$

multiplied by the amplitude of the incident wave at the point at which the element of volume is situated. V is the potential energy that an electron would have at that point. A rigid proof of this law will be given in the next chapter (Section II), depending on the wave equation that these waves can be shown to satisfy. But if we assume, as is the case for light, that each element of volume scatters a wavelet, and that the amplitude of the wave scattered depends only on the "refractive index" $\sqrt{E/(E-V)}$ at that point, then this law may be proved without the help of the wave equation. We may do this by taking an *isolated* element of volume, in which V is different from zero, and calculating the wave that it will scatter by putting in the boundary conditions, and then arguing that the contribution of this element to the total scattered amplitude must be the same whether the element

is isolated or not. It is important to realise that this method does involve an assumption, for in the case of light there is a definite mechanism that causes the scattering, whereas in the case of de Broglie waves none is known.

That the amplitude of the wave scattered by an element of volume $dxdydz$ is given by (5) is most directly proved by taking a spherical element of volume, with V equal to zero outside, but differing from zero inside, and putting in boundary conditions. The calculation, however, involves spherical harmonics; the result can be obtained by the use of more elementary analysis by the following method. We imagine a plane wave of unit amplitude falling normally on a thin plate, with a potential jump at its two edges. We suppose that V, the potential energy of an electron, is equal to K inside the plate, and to zero outside. Let the surfaces of the plate be the planes $z = 0$, $z = l$. Then we shall have

$$\begin{aligned} V &= 0, \qquad z < 0, \\ V &= K, \qquad 0 < z < l, \\ V &= 0, \qquad z > l. \end{aligned}$$

To obtain the amplitude a of the wave reflected by the plate, we set for the wave function

$$\begin{aligned} \psi &= e^{-2\pi iNz} + a e^{2\pi iNz}, && z < 0, \\ \psi &= b e^{-2\pi iN'z} + c e^{2\pi iN'z}, && 0 < z < l, \\ \psi &= d e^{-2\pi iNz}. && z > l. \end{aligned}$$

N, as before, is the wave number in free space, N' in the medium. The time factor $e^{2\pi i\nu t}$ is omitted. Putting in the boundary conditions, we obtain

$$\begin{aligned} 1 + a = b + c, \qquad 1 - a &= \frac{N'}{N}(b - c), \\ b e^{-2\pi iN'l} + c e^{2\pi iN'l} &= d e^{-2\pi iNl}, \\ b e^{-2\pi iN'l} - c e^{2\pi iN'l} &= \frac{N}{N'} d e^{-2\pi iNl}. \end{aligned}$$

We now make the assumption that l is very much less than the wave length, so that the exponentials can be replaced by the

first two terms in their expansion. Solving these equations for a, the amplitude of the wave reflected by the plate, we obtain

$$a = \pi i l\,(N^2 - N'^2)/N \qquad \ldots\ldots(6).$$

Now, our assumption is that this reflection is caused by each element of volume in which V is different from zero scattering a wavelet, and we wish to find the amplitude of the wave scattered by an element of volume $dxdydz$. Let this be $A\,dxdydz/R$. Then each element of area dS of the plate scatters a wavelet of amplitude $lA\,dS/R$. By a known theorem, these wavelets interfere to form a plane wave of amplitude

$$il\,A\lambda,$$

where λ is the wave length of the waves in free space. The factor i in the amplitude denotes the fact that the phase of the resultant wave is a quarter of a period greater than that of the spherical wavelets of which it is formed. Equating with (6), we obtain that

$$\begin{aligned} A &= \pi\,(N^2 - N'^2) \\ &= 2\pi m V/h^2, \end{aligned}$$

which is the result that we set out to prove. We have then that if a wave falls on a region in which V is different from zero, each element of volume $dxdydz$ scatters a wavelet, whose amplitude at distance R from the element is

$$\frac{1}{R}\,\frac{2\pi m V}{h^2}\,dxdydz$$

times the amplitude of the wave at that point.

This result will now be used to calculate the scattering of electrons by atoms.

SECTION IV

THEORY OF SCATTERING

The experimental fact upon which we have based our theories is that de Broglie waves are scattered from atoms, and that the waves scattered from different atoms can interfere with each

other. It is therefore particularly important to obtain a qualitative description of the scattering. We require to know the amplitude of the wave scattered in any direction by an atom. From this we can deduce the number of electrons that will be scattered into a given solid angle by an atom, when a beam of electrons of given intensity falls upon it.

Now an atom is a complicated system, consisting of one or more electrons moving in the field of the nucleus. However, for a great many purposes the atom behaves as though it were a static distribution of electric charge. The reason for this will be discussed in Chapter IV. Here we need only state that there are certain numerical methods by which the effective charge distribution can be calculated; in particular, the hydrogen atom behaves as if the charge density at distance r from the nucleus were

$$\epsilon\rho\,(r) = \frac{\epsilon}{\pi a^3}\, e^{-2r/a},$$

where ϵ is the charge on an electron, and a is the radius of the ground orbit in Bohr's theory of the atom. We assume that the atom scatters as though it were such a distribution of charge, an assumption that will be justified in Chapter VII. This charge distribution, together with the charge on the nucleus, will produce a field; we denote the potential of an electron in this field by $V\,(r)$.

The presence of the field, as we have stated, acts on de Broglie waves in much the same way as a speck of refracting matter acts on light waves. As we have shown, each element of volume $dxdydz$ scatters a wavelet of amplitude

$$\frac{2\pi m}{h^2}\, V\,dxdydz/R$$

times the amplitude of the wave at this point. To obtain the amplitude of the total scattered wave, we must consider the interference of these wavelets.

If the refractive index caused by the field is only slightly different from unity, and if the field only extends over a volume

of dimensions not much larger than the wave length, then it is clear that the amplitude and phase of the incident wave will be very little distorted by the field, and will be almost the same as they would be if the field were not there. In this case it is particularly simple to calculate the amplitude of the scattered wave, for the phase with which each wavelet starts is just that of the incident wave, and its amplitude is also given by that of the incident wave. The wave resultant from all these scattered wavelets can be calculated from a well-known formula, which can be stated as follows. Suppose that a wave of unit amplitude and wave length λ falls on a piece of some scattering medium, and suppose that the amplitude and phase of the wave are sensibly the same as they would be if the medium were not there. We suppose that the scattering medium is spherically symmetrical, and that an element of volume at distance r from its centre will scatter a wavelet of amplitude $P(r)\,dx\,dy\,dz/R$ at distance R from the element. Then the amplitude of the resultant wave scattered in the direction θ is

$$f(\theta)/R$$

at a large distance R from the scattering centre, where

$$f(\theta) = 4\pi \int_0^\infty \frac{\sin \mu r}{\mu r} P(r)\, r^2 dr \qquad \text{.....(7)}$$

and

$$\mu = 4\pi \sin \tfrac{1}{2}\theta/\lambda.$$

The formula is much used in X-ray analysis. We give a proof in the Appendix*.

The formula can at once be applied to the scattering of de Broglie waves by atoms. The amplitude of the scattered wave will be given by (7), where

$$P(r) = \frac{2\pi m}{h^2} V(r) \qquad \text{.....(8).}$$

The integral is more conveniently expressed in terms of the

* Appendix, Note 2.

charge density $\rho\,(r)$, rather than the potential V. Transforming by partial integration we obtain *

$$f(\theta) = \frac{\epsilon^2}{2mv^2}(Z - F)\,\mathrm{cosec}^2\,\tfrac{1}{2}\theta \qquad \ldots\ldots(9),$$

where

$$F = 4\pi \int_0^\infty \frac{\sin \mu r}{\mu r}\,\rho\,(r)\,r^2 dr \qquad \ldots\ldots(10).$$

For the case of the hydrogen atom, this reduces to

$$f(\theta) = \frac{h^2}{8\pi^2 m\epsilon^2}\left\{\frac{1}{1+z^2} + \frac{1}{(1+z^2)^2}\right\},$$

where

$$z = \mu a.$$

The number of electrons scattered into a given solid angle when a stream of electrons falls on an atom can at once be deduced. If the incident beam has unity density, then the scattered beam represents a density of $R^{-2}\,|\,f\,(\theta)\,|^2$ at distance R from the atom. Thus if N electrons in the incident beam cross unit area per unit time, the number scattered per unit time through an angle θ into the solid angle $d\omega$ is

$$N\,|\,f\,(\theta)\,|^2\,d\omega.$$

SCATTERING OF α PARTICLES BY NUCLEI

An α particle has nearly 7000 times the mass of an electron, and therefore, if it collides with an atom, it will hardly be affected by the electrons. If it suffers deflection, therefore, the deflection must be due to the field of the nucleus. According to the classical mechanics, if the α particle and the nucleus are simply charged particles with charges $Z'\epsilon$, $Z\epsilon$, so that their potential energy in one another's field is $ZZ'\epsilon^2/r$, and if also the nucleus is so much heavier than the α particle that its recoil may be neglected, then the effective cross-section that must be hit by an α particle, if it is to be scattered into a solid angle $d\omega$, is

$$\left(\frac{ZZ'\epsilon^2}{2Mv^2}\right)^2 \mathrm{cosec}^4\,\tfrac{1}{2}\theta\,.d\omega \qquad \ldots\ldots(11).$$

* Appendix, Note 3.

M is here the mass of an α particle, and v is its velocity. The formula was first deduced by Rutherford, and, for the heavier nuclei, is in agreement with experiment. For the lighter nuclei it is not, even when allowance has been made for the motion of the nucleus when struck. It is deduced that, at very close distance, there is a departure from the inverse square law of force.

Now streams of α particles, as well as streams of electrons, may be expected to behave as beams of waves, only the wave length in this case will be h/Mv. This is very much smaller than that for electrons of the same velocity, and the wave nature is therefore very difficult to detect. It could perhaps be observed experimentally, by reflecting a beam of α particles from a crystal surface upon which they impinge at a very oblique angle. But whatever the wave length, if the beam does behave as a beam of waves, the scattering of the α particles should be determined by the scattering of these waves, given by the formulae (7) and (8). If the wave mechanics is in agreement with experiment, then (7) should lead to just the Rutherford formula (11). We shall find that it does.

The effective cross-section that must be hit by an α particle if it is to be scattered into the solid angle $d\omega$ is, according to the wave mechanics,

$$|f(\theta)|^2 d\omega,$$

where $f(\theta)$ is given by (7) and (8), with

$$V(r) = ZZ'\epsilon^2/r.$$

However, the integral (7) does not converge. This is actually due to the fact that the condition on which the formula (7) depends, that the amplitude and phase of the incident wave should be unaltered by the presence of the field, is not strictly true. If these alterations were taken into account, the integral would converge. However, a value of $f(\theta)$ can be obtained more simply by recognising that when the α particle is a long way from the

nucleus it is shielded from its field by the electrons, so that the potential is more correctly represented by

$$\frac{ZZ'\epsilon^2}{r} e^{-r/a},$$

where a is a length of the order of magnitude of the radius of the atom.

If we now evaluate the integral, we obtain

$$f(\theta) = \frac{ZZ'\epsilon^2}{2Mv^2} \operatorname{cosec}^2 \tfrac{1}{2}\theta \,.\, 1/[1 + (\mu^2 a^2)^{-1}].$$

a is very large compared to the wave length, and so this reduces to

$$f(\theta) = \frac{ZZ'\epsilon^2}{2Mv^2} \operatorname{cosec}^2 \tfrac{1}{2}\theta,$$

which yields the Rutherford formula. A more rigorous method of obtaining this formula will be discussed in the next chapter.

We have here therefore a case in which classical mechanics and wave mechanics give the same result. The inverse square law field is unique in this respect. For all other fields that have been investigated, the two different theories give quite different results.

COMPARISON BETWEEN SCATTERING OF X-RAYS BY AN ATOM, AND THE SCATTERING OF ELECTRONS

In calculating the scattering of X-rays by an atom, it is assumed that if a beam of X-rays of unit amplitude falls on an atom, each element of charge $\epsilon d\rho$ in the atom scatters a wavelet of amplitude

$$\frac{\epsilon^2 d\rho}{mc^2} \Big/ R.$$

ϵ/m is the ratio of the charge of an electron to its mass, which, in deriving the formula, is considered to be the ratio between the charge and mass of each little element of charge. The wave-

lets interfere with each other. The amplitude of the scattered wave is clearly given by

$$\frac{\epsilon^2}{mc^2} F(\theta) \qquad \text{.....(12),}$$

where $F(\theta)$ is given by (10).

In calculating the scattering of de Broglie waves, on the other hand, we assumed that the potential in each element of volume, not the charge, determined the amplitude of the wave scattered. The similarity between the formulae (12) and (9) calls therefore for some comment.

It is clear that the formula (9) would be obtained if we assume that the amplitude of the wave scattered by each element of volume *is* proportional to the charge that it contains, and in fact equal to $\frac{\epsilon^2 d\rho}{2mv^2}$ $\operatorname{cosec}^2 \frac{1}{2}\theta$ times the amplitude of the wave at that point, and that the nucleus also scatters a wave amplitude $\frac{Z\epsilon^2}{2mv^2}$ $\operatorname{cosec}^2 \frac{1}{2}\theta$. These waves have opposite phases, since V is positive in the one case and negative in the other. Their interference produces a wave of amplitude given by (9). We have therefore an alternative way of picturing the scattering, in which we consider that each element of charge scatters a wave of just the amplitude that an isolated element of charge would, according to the Rutherford formula.

CHAPTER II

THE WAVE EQUATION

SECTION I

In this chapter we are concerned with the wave equation satisfied by de Broglie waves. In order to show the various types of equation possible, we shall discuss three familiar types of wave motion, namely, the vibrations of a string, sound waves in a gas, and light waves. Each of these will be found to illustrate certain properties of de Broglie waves.

Consider a string of density, or mass per unit length, equal to ρ. Let us assume that ρ is not the same for all points, but varies with x, the distance along the string. Let T be the tension of the string, and y the displacement at any point. We shall only deal with small displacements, that is to say, those for which $\frac{\partial y}{\partial x}$ is small compared to unity.

Consider any element dx of the string, and let y be its displacement. Then the force acting on the element is, to the order to which we are working,

$$T\frac{\partial^2 y}{\partial x^2}.$$

The mass of the element is ρdx; so, $\frac{\partial^2 y}{\partial t^2}$ being its acceleration, we have

$$\rho\frac{\partial^2 y}{\partial t^2} = T\frac{\partial^2 y}{\partial x^2} \qquad \text{.....(1).}$$

This equation is of the second order in t. Therefore, if we know y and $\frac{\partial y}{\partial t}$ initially, the wave disturbance is known for all time.

We shall find it convenient, in order to compare the wave equation (1) with other wave equations, to replace it by a pair of simultaneous equations both linear in $\frac{\partial}{\partial t}$. If v be the velocity

with which any point of the string is moving, then (1) is equivalent to

$$\left.\begin{aligned} \rho \frac{\partial v}{\partial t} &= T \frac{\partial^2 y}{\partial x^2} \\ \frac{\partial y}{\partial t} &= v \end{aligned}\right\} \qquad \text{.....(2).}$$

By a monochromatic wave, or wave of given frequency ν, we mean a wave such that every point of the string executes a simple harmonic motion of frequency ν. For all x, then, y will satisfy the differential equation

$$\frac{\partial^2 y}{\partial t^2} + 4\pi^2\nu^2 y = 0 \qquad \text{.....(3).}$$

It follows from (1) and (3) that, in a monochromatic wave, y satisfies the further equation

$$4\pi^2\nu^2 \frac{\rho}{T} y + \frac{\partial^2 y}{\partial x^2} = 0 \qquad \text{.....(4).}$$

It is clear from equation (4) that $\frac{1}{\nu}\sqrt{\frac{T}{\rho}}$ is the wave length of these waves. A variation in ρ causes a change in wave length, or in other words a "refraction" of any wave disturbance that may travel along the string.

We may write (4)

$$\frac{\partial^2 y}{\partial x^2} + 4\pi^2 N^2 y = 0 \qquad \text{.....(5),}$$

where N is the wave number at any point for waves of the given frequency. If the density of the string is not uniform, then N is a function of x.

It is interesting to see what form a monochromatic wave will have if the density of the string changes discontinuously at a point $x = a$ from the value ρ_1 to the value ρ_2. It is clear that y, the displacement, will be continuous, and from equation (4) we

see that $\frac{\partial y}{\partial x}$ will also be continuous; for

$$\frac{\partial y}{\partial x} = -\frac{4\pi^2\nu^2}{T}\int^x \rho y\, dx,$$

and though ρ may change discontinuously, the value of the integral will not. These waves, therefore, satisfy the same boundary conditions as de Broglie waves at a point where the refractive index changes discontinuously; if y is plotted against x, there is no "kink" in the curve.

Not all waves satisfy these boundary conditions; we have seen already that sound waves do not. It is interesting to compare the wave equation for sound with (5), and to see in what way the equations differ. Let us consider a sound wave moving along the z-axis, in a gas of varying mean density. Let $\dot{y}$ be the velocity with which a given group of molecules of the gas is moving. The rate at which the density at any point decreases is equal to the flow away from that point. We have, therefore, if ρ be the density,

$$\frac{\partial \rho}{\partial t} + \rho\frac{\partial \dot{y}}{\partial z} = 0 \qquad \text{.....(6).}$$

Further, the force on any group of molecules of volume $d\tau$ is $-\frac{\partial p}{\partial z}d\tau$, and therefore

$$\rho\frac{d\dot{y}}{dt} + \frac{\partial p}{\partial z} = 0 \qquad \text{.....(7).}$$

From these two equations we obtain

$$\frac{\partial}{\partial z}\left(\frac{1}{\rho}\frac{\partial p}{\partial z}\right) = \frac{d}{dt}\left(\frac{\dot{\rho}}{\rho}\right) \qquad \text{.....(8).}$$

Further, p and ρ are connected by the relation

$$p = C\rho^{\gamma}.$$

Therefore, differentiating this equation logarithmically,

$$\frac{\partial}{\partial t}\left(\frac{\dot{\rho}}{\rho}\right) = \frac{1}{\gamma}\frac{\partial}{\partial t}\left(\frac{\dot{\rho}}{\rho}\right).$$

Therefore (8) reduces to

$$\frac{\partial}{\partial z}\left(\frac{1}{\rho}\frac{\partial p}{\partial z}\right)=\frac{1}{\gamma}\frac{\partial}{\partial t}\left(\frac{\dot{p}}{p}\right) \qquad \text{.....(9).}$$

Now the variations of p, ρ at any point are very small compared to the mean pressure and density p_0, ρ_0. Therefore (9) may be written

$$\frac{\partial}{\partial z}\left(\frac{1}{\rho_0}\frac{\partial p}{\partial z}\right)=\frac{1}{p_0\gamma}\ddot{p}.$$

Let now $$p = p_0 + P.$$

Then for a wave of frequency ν we have

$$P+\frac{p_0\gamma}{4\pi^2\nu^2}\frac{\partial}{\partial z}\left(\frac{1}{\rho_0}\frac{\partial P}{\partial z}\right)=0 \qquad \text{.....(10),}$$

which is the required equation.

At a boundary, where ρ_0 changes, we have

$$\frac{1}{\rho_0}\frac{\partial P}{\partial z}=-\int^z\frac{4\pi^2\nu^2}{p_0\gamma}P\,dz.$$

The right-hand side must be continuous; the boundary condition is therefore that

$$\frac{1}{\rho_0}\frac{\partial P}{\partial z}$$

shall be continuous, which is the result that we found in the last chapter.

A third example of wave motion with which we may compare de Broglie waves is afforded by electromagnetic wave motion. The state of the medium is described by two vectors **E** and **H**. In free space, in the absence of charge, **E** and **H** satisfy two equations linear in the time

$$\left.\begin{aligned}\frac{\partial \mathbf{E}}{\partial t} &= \quad c\ \mathrm{curl}\ \mathbf{H}\\ \frac{\partial \mathbf{H}}{\partial t} &= -c\ \mathrm{curl}\ \mathbf{E}\end{aligned}\right\} \qquad \text{.....(11).}$$

The energy density in the medium is $\frac{1}{2}(\mathbf{E}^2+\mathbf{H}^2)$.

Now let us return to the de Broglie waves that describe the behaviour of a beam of electrons. We do not know of any medium that is vibrating, all we know is that something vibrates, and that more electrons are found at points where the amplitude of these vibrations is great than at points where it is small. We therefore describe the state of the wave by two scalar functions $f(x, y, z)$ and $g(x, y, z)$. These functions may be thought of as analogous either to **E** and **H** in a light wave, or to the displacement and velocity of the medium in a sound wave. (It must be stressed that they are not in the least analogous to the position and velocity of the electrons that they represent.) They must further satisfy a pair of wave equations that determine the way in which a wave disturbance is propagated through space. If these waves are to behave in at all the same way as the other kinds of wave motion known to physics, these equations must be linear in the time.

For the present we shall confine ourselves to the monochromatic wave trains that we have used to describe continuous streams of electrons. We have found that the wave number N of these waves in an electric field is $\sqrt{2m(E-V)}/h$, where E is the energy of each electron, and V is its potential energy at the point considered. Further, in order to ensure that our waves do not predict a creation of charge when they are reflected from a potential jump, we have postulated that f, $\frac{\partial f}{\partial n}$ and g, $\frac{\partial g}{\partial n}$ shall always be continuous at a potential jump. It follows that f and g will satisfy an equation of the type (5) rather than of the type (10); thus, putting in the expression for the wave number, we obtain for the equations, satisfied by the wave that describes a stream of electrons of energy E,

$$\nabla^2 f + \frac{8\pi^2 m}{h^2}(E - V) f = 0 \qquad \text{.....(11.1),}$$

$$\nabla^2 g + \frac{8\pi^2 m}{h^2}(E - V) g = 0 \qquad \text{.....(11.2).}$$

We stated in Chapter I that the square of the amplitude of

these waves was to be equal to the density of electrons at any point. This we may now make more precise. In the case of light waves, the energy density in the medium is equal to $\frac{1}{2}(\mathbf{E}^2 + \mathbf{H}^2)$, and the density of light quanta is therefore equal to $\frac{1}{2}(\mathbf{E}^2 + \mathbf{H}^2)/h\nu$. Let us assume that, analogously, the density of electrons in a de Broglie wave is proportional to $f^2 + g^2$. Let us choose the units in which the wave displacement is measured so that the electron density is *equal* to

$$f^2 + g^2.$$

Then $(f^2 + g^2)\, d\tau$ is the probability that an electron is in the volume element $d\tau$.

In a monochromatic light wave, $\mathbf{E}$ and $\mathbf{H}$ describe waves in phase with one another. Therefore the energy density at a given point is not constant, but fluctuates with the frequency of the wave. The probability, therefore, that a light quantum shall be found in any volume element fluctuates also. The theory of de Broglie waves in use at the present time has been built up on the assumption that for them this is not so, but that the electron density at any point in a monochromatic wave is strictly a constant. The author does not know whether it is necessary to make this assumption in order to predict the experimental results that have been deduced from the wave mechanics. It is in any case convenient to do so. It follows from this assumption that, in a plane wave, f and g must be a quarter of a period apart, so that if

$$f = a \cos 2\pi (\nu t - z/\lambda),$$

then

$$g = a \sin 2\pi (\nu t - z/\lambda),$$

so that we have

$$f^2 + g^2 = a^2,$$

which does not fluctuate with the time.

Following the usual custom among workers on the wave mechanics, we shall use instead of the pair of real functions f and g, the single complex function

$$\psi = f + ig.$$

The pair of equations (11) then reduces to the single equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 \qquad \ldots\ldots(12),$$

which is the original equation of Schrödinger. The density of electrons $f^2 + g^2$ becomes

$$|\psi|^2,$$

and the equation of a plane wave travelling along the z-axis, representing a stream of electrons containing a^2 per unit volume, becomes

$$\psi = a\, e^{2\pi i\nu t}\, e^{2\pi i z/\lambda + \alpha},$$

where α is an arbitrary phase. The equation of the most general monochromatic wave will be

$$\psi = e^{2\pi i\nu t} f(xyz) \qquad \ldots\ldots(12.1),$$

where f is any, possibly complex, function. ψ must have this form in order that $|\psi|^2$ shall not vary with the time.

SECTION II

THE THEORY OF SCATTERING

We have already found, using certain approximations, the amplitude of the de Broglie wave scattered by a centre of force, such as a nucleus or an atom. In this calculation we made use of the law that each element of volume scattered a wavelet of amplitude

$$\frac{2\pi m}{h^2} V(xyz)\, dx dy dz/R$$

times the amplitude of the wave at that point. This law was deduced from the assumption that the wavelet scattered by each element of volume depended only on the potential at that point. Now that we know the wave equation satisfied by these waves it is possible to deduce this law rigorously, without making any such assumption.

Let us try to find a solution of the wave equation (12) that does represent the scattering. We wish to find a solution that

represents an incident wave falling on the atom, together with a scattered wave flowing away from the atom. Suppose that the incident wave moves along the z-axis. Omitting the time factor, $\exp(2\pi i\nu t)$, the incident wave should have the form $\exp(-2\pi iz/\lambda)$, and the scattered wave the form $r^{-1}f(\theta\phi) \cdot \exp(-2\pi ir/\lambda)$. $f(\theta\phi)$ is then the amplitude of the scattered wave, in a direction specified by the polar angles $\theta\phi$. $|f(\theta\phi)|^2 d\omega$ is the number of electrons scattered, per unit time, in this direction into the solid angle $d\omega$, if, in the incident beam, one electron crosses unit area per unit time.

By a well-known theorem, if ζ is any function, a solution of the equation

$$(\nabla^2 + k^2)\psi = \zeta(xyz) \qquad \text{.....(13),}$$

is

$$\psi = \frac{1}{4\pi}\iiint \frac{e^{-ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\zeta(x'y'z')\,dx'dy'dz' \qquad \text{.....(14).}$$

$\mathbf{r}$ is the vector xyz, $\mathbf{r}'$ the vector $x'y'z'$. This function represents the disturbance obtained by considering the resultant of wavelets of amplitude

$$\frac{1}{4\pi}\zeta(xyz)\,dxdydz/R,$$

and wave length $2\pi/k$, spreading out from each element of volume. The most general solution of (13) is obtained by adding to (14) the most general solution of

$$(\nabla^2 + k^2)\psi = 0 \qquad \text{.....(15).}$$

Now the wave equation (12) may be written

$$(\nabla^2 + k^2)\psi = \frac{8\pi^2 m}{h^2} V\psi,$$

where

$$k^2 = \frac{8\pi^2 mE}{h^2}.$$

It follows that the most general solution of the wave equation satisfies the "integral equation"

$$\psi = \psi_0 + \iiint \frac{2\pi m}{n^2} V(x'y'z') \frac{e^{-ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\psi(x'y'z')\,dx'dy'dz' \qquad \text{.....(16),}$$

where ψ_0 is the general solution of (15). If now we take $\psi_0\,(xyz)$ equal to e^{-ikz}, then the right-hand side of (16) represents an incident wave, together with a scattered wave, and is therefore the wave function that describes the scattering. But the scattered wave in (16) is the wave that would be formed if each element of volume scattered a wavelet of amplitude

$$\frac{2\pi m}{h^2}\, V\,(xyz)\,\psi\,(xyz)\,dxdydz/R \qquad \ldots\ldots(17),$$

which is what we set out to prove.

Our assumption therefore as to the amplitude of the wave scattered by each element of volume follows directly from the wave equation. The approximation, that the wave is not much distorted within the atom, amounts to setting ψ in (17) equal to ψ_0, that is, to e^{-ikz}. If the integral in (16) were then evaluated (for large r), the results of Chapter I would follow.

In principle it is possible to find a solution of the wave equation representing an incident wave and a scattered wave, without making the approximation that the wave is but little deformed inside the atom. In general the amplitude of the scattered wave cannot be expressed in terms of tabulated functions, and the calculations required to evaluate it are laborious. In the case of the inverse square law field, however, an exact solution can be found; it is found that*

$$|\,f\,(\theta)\,|^2 = (Z\epsilon^2/2mv^2)^2\,\mathrm{cosec}^4\,\tfrac{1}{2}\theta$$

exactly, where Ze is the charge on the nucleus.

Rutherford's scattering law is therefore true exactly for the inverse square law field, on the wave mechanics as on the classical theory.

SECTION III

REFLECTION OF DE BROGLIE WAVES

We have remarked that de Broglie waves are refracted by an electrostatic field and that the refractive index is $\sqrt{E/(E-V)}$, E being the energy of the electrons that the waves represent. Now if $V > E$, the refractive index becomes imaginary. This

* Cf. Temple, *Proc. Roy. Soc.* A, vol. CXXI, p. 673 (1928).

only happens in parts of the field where, according to the classical theory, the electrons could not go at all; they would be reflected at the boundary of such a region. We shall now discuss, in a simple case, the behaviour of de Broglie waves at such a boundary.

Let us suppose that a beam of cathode rays passes through a grid and enters a uniform field, such that the force on the electrons is in a direction opposite to their motion. Then, according to the classical theory, the electrons will be slowed down, and at a certain point turned back, and will return through the grid with a velocity equal and opposite to that which they had before. We shall now show that the wave equation predicts almost the same thing, though there is a certain difference between the two descriptions that is of very great interest.

The wave equation in question is

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0,$$

where

$$V = 0, \qquad z < 0,$$
$$= az, \qquad z > 0.$$

The electrons are supposed to be moving along the z-axis. The transverse dimensions of the beam are irrelevant to our problem, and it will simplify the mathematics if we take an infinite beam, the density being uniform in the xy-plane. Then ψ will be a function of z, t only, and ∇^2 can be replaced by $\frac{\partial^2}{\partial z^2}$. Omitting the time factor $e^{2\pi i\nu t}$, we have for the incident wave

$$\psi = e^{-2\pi iNz},$$

and for the reflected wave

$$\psi = e^{2\pi iNz} \qquad \text{.....(18).}$$

With N equal to $\sqrt{2mE/h}$, these two values of ψ are independent solutions of the wave equation in the region for which $z < 0$, that is to say, to the left of the grid.

To the right of the grid, the solutions will be of the same form

but the wave number N will now be a function of z. In any small interval of length, then, in which az is sensibly constant, two independent solutions are given by (18) with

$$N = \sqrt{2m\,(E - az)}/h.$$

These two functions represent incident and scattered waves of slowly increasing wave length, until we come to the point $x = E/a$, where, according to the Newtonian mechanics, the electrons are turned back. To the right of this point, two independent solutions are

$$e^{\pm\gamma z},$$

where $$\gamma = 2\pi\sqrt{2m\,(az - E)}/h.$$

One solution rises exponentially for increasing z, the other falls away exponentially.

Now let us consider the solution of the wave equation in the whole range of z. The equation is a linear equation of the second order, and therefore has two independent solutions. These solutions may be obtained by means of Bessel functions, but we may obtain their general character by more elementary methods.

We wish to find a solution that will describe what will happen when a stream of electrons falls on a repulsive electric field. We must therefore choose the solution that, for $z > E/a$, decreases exponentially for increasing z. The solution that increases exponentially predicts ever-increasing density of electrons, and therefore cannot be the correct wave function to describe what is happening.

The condition, then, that the wave function must fall off exponentially for $z > E/a$, determines which of the two solutions to take. We now enquire what the form of the solution will be for $z < E/a$, that is to say, we wish to know, in any small interval, what combination of the two solutions (18) will represent the required wave function. In order to answer this question completely, we should have to solve the wave equation, but we can see at once that the required solution must be

everywhere real (omitting the factor $e^{2\pi i\nu t}$), for ψ is real to the right of the point $z = E/a$, and therefore must be real everywhere. The solution in any small interval will therefore be

$$\psi = A \cos 2\pi (Nz + \epsilon),$$

with N equal to $\sqrt{2m(E - az)}$, and A and ϵ an amplitude and phase that are constant in any small region of the order of magnitude of a wave length, but are not constant over the whole range. Putting in the time factor, we have

$$\begin{aligned}\psi &= Ae^{2\pi i\nu t} \cos 2\pi (Nz + \epsilon) \\ &= \tfrac{1}{2}Ae^{2\pi i(\nu t + Nz + \epsilon)} + \tfrac{1}{2}Ae^{2\pi i(\nu t - Nz - \epsilon)} \qquad \text{.....(19).}\end{aligned}$$

The wave function, therefore, represents an incident and a reflected wave, of equal amplitude.

The wave mechanics, therefore, predicts that all the electrons are reflected, just as the Newtonian mechanics does; but there is this difference, that whereas according to the Newtonian mechanics all the electrons are turned back exactly at the point $x = E/a$, according to the wave theory some must get beyond it; for there is a density of electrons $e^{-2\gamma z}$, which does not quite vanish however far along the z-axis we go. γ^{-1} is a very small length indeed, of the order of the de Broglie wave length; not more than one electron in 10^{10} will penetrate 1 mm. beyond the point $x = E/a$ (calculated for 100-volt electrons, field of 100 volts per cm.). So the divergence between the two theories is quite negligible in any ordinary experiment. Nevertheless, this property of the wave mechanics has an application to physics, as we shall see in Chapter IV, when we consider the artificial disruption of the nucleus by an α particle. The repulsive field is then the inverse square law repulsion between the α particle and the nucleus; and we shall find that, whereas according to the Newtonian mechanics all α particles are turned back before they get far enough to cause disruption, according to the wave mechanics a small number do get further in.

CHAPTER III

GROUP VELOCITY AND THE UNCERTAINTY PRINCIPLE

SECTION I

THE FREQUENCY OF DE BROGLIE WAVES

Up till the present we have been concerned only with phenomena in which there is a steady flow of particles. These particles we have described by monochromatic trains of waves. We shall now generalise the wave mechanics, in order to enable it to describe phenomena in which the flow of particles at any point is not steady. This will be the case if, for example, a beam of electrons is fired at a screen in which there is an aperture that is initially closed, and then opened for a short time, and then closed again. If this experiment were carried out, a cluster, or cloud of electrons would pass through the aperture and travel out into space. The velocity with which the whole cluster would travel would of course be equal to v, the actual velocity with which the electrons were fired at the aperture. A rather roundabout way of describing what happens is to say that a *region*, in which the electron density is different from zero, is travelling through space, with velocity equal to v.

The wave mechanics can very easily describe the motion of this cloud of electrons. Let us consider what will happen when any train of *waves* falls on an aperture that is open for a short time only, and then is closed again. A "wave packet" passes through the aperture and travels out into space. A wave packet, or wave group, is the name we give to a wave disturbance that is confined to a limited volume of space. The displacement, in a wave packet, plotted against the direction in which the waves are moving, will look somewhat as shown in Fig. 4. The velocity with which the wave packet as a whole travels is called the

"group velocity." The group velocity is not in general equal to the wave velocity, the velocity with which the crest of each wave travels. If ν be the frequency of the waves, and N the wave number, then, as is well known, the group velocity is equal to $\frac{d\nu}{dN}$. If the waves are light waves in free space, then the group velocity *is* the same as the wave velocity, for we have

$$\nu = cN,$$

and therefore

$$\frac{d\nu}{dN} = c;$$

but for waves whose wave velocity depends on the frequency, this is no longer the case.

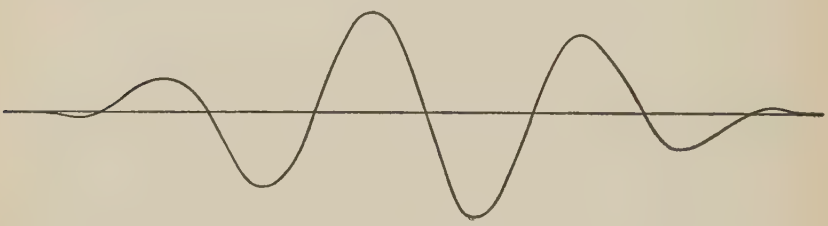


Fig. 4.

We have not yet been able to attach any physical significance to the frequency of de Broglie waves; only the wave length is measurable by direct experiment. However, we now see that the group velocity of these waves must be identified with the velocity of the electrons that they are intended to represent. For we have assumed that, in any experiment, the density of electrons will be correctly determined by the square of the amplitude of a de Broglie wave, so if the wave packet (which is simply a region in which the amplitude is different from zero) is to represent the motion of the cluster correctly, then we must have

$$\frac{d\nu}{dN} = v \qquad \text{.....(1).}$$

Now v, the velocity of the electrons, is equal to hN/m, so that (1) reduces to

$$\frac{d\nu}{dN} = hN/m.$$

Integrating this equation, we obtain

$$\nu = \tfrac{1}{2}hN^2/m + C \qquad \text{.....(2),}$$

or, in terms of v, $$\nu = \tfrac{1}{2}mv^2/h + C \qquad \text{.....(3).}$$

C in equations (2) and (3) is an arbitrary constant. Owing to the fact that the frequency never enters any physical problem except as $\frac{d\nu}{dN}$, or as the difference between two frequencies, the value that is assigned to this constant does not affect any physical result. It is convenient to put it equal to zero.

We have shown then that wave groups of de Broglie waves do behave like clusters of electrons, if ν, the frequency of the waves, is given by the equation

$$h\nu = \tfrac{1}{2}mv^2.$$

The proof that we have given is only valid in space in which there is no electrostatic field. It can, however, easily be extended. We can show that wave groups do behave as electrons actually would in electrostatic fields. For we have already shown that a beam of de Broglie waves will follow the same path as a beam of electrons actually would (Chapter I, Section II), and a wave packet would follow the same path as the steady beam. We have only to show, therefore, that the velocity with which the wave packet moves is at all points the same as that with which the cluster of electrons would move.

We have shown that the frequency of the waves is equal to the kinetic energy of the electrons in free space divided by h; therefore, in a field we must have

$$E = h\nu \qquad \text{.....(4),}$$

where E is the total energy of the electrons. The wave number of the waves in the field is, as we know, given by

$$N = \sqrt{2m\,(E - V)}/h.$$

Therefore, expressing the frequency in terms of the wave number, we have

$$\nu = (N^2h^2/2m + V)/h,$$

and therefore, for the group velocity,

$$\frac{d\nu}{dN} = \frac{Nh}{m}.$$

This is equal to the velocity v that the cluster of electrons ought to have, according to the classical theory.

We conclude, therefore, that a wave packet in an electrostatic field behaves just as a cluster of electrons actually would, provided of course that the fields are not atomic fields, but slowly varying ones that remain sensibly constant in a distance comparable with a wave length.

SECTION II

THE WAVE EQUATION FOR NON-MONOCHROMATIC WAVES

The wave equations obtained in the last chapter are only applicable to the monochromatic wave trains that describe steady beams of electrons. We now require an equation that a disturbance such as a wave packet, that is not strictly monochromatic, will satisfy. Since ψ, or rather its real and imaginary parts, f and g, constitute a wave disturbance, f and g must satisfy a pair of equations linear in the time, analogous to (2) or (11) of Chapter II.

Now we found in Chapter II, equation (12.1), that the most general monochromatic disturbance possible had a wave function of the form

$$\psi = e^{2\pi i\nu t} f(xyz) \qquad \ldots\ldots(5.1),$$

where f satisfies Schrödinger's equation (12), which, by virtue of (4) may be written

$$\nabla^2 f + \frac{8\pi^2 m}{h^2}(h\nu - V)\psi = 0.$$

Now the most general possible disturbance will be obtainable by adding together monochromatic disturbances, and will therefore be of the form

$$\Sigma_n f_n e^{2\pi i \nu_n t} \qquad \ldots\ldots(5.2).$$

From (5.1) and (5.2) it is clear that this wave function satisfies the equation

$$\frac{ih}{2\pi}\frac{\partial \psi}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2\psi - V\psi \qquad \ldots\ldots(6).$$

Since this equation is linear in the time, it is the equation required.

This is the general wave equation, analogous to Maxwell's equations for light waves, satisfied by the wave function. Expressed in terms of the real and imaginary components of ψ, it becomes

$$\frac{h}{2\pi}\frac{\partial f}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2 g - Vg,$$

$$-\frac{h}{2\pi}\frac{\partial g}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2 f - Vf.$$

The equations differ from Maxwell's, firstly in that they describe a scalar wave disturbance, and secondly in that they contain the operator ∇^2 instead of the linear operator "curl." This expresses the fact that the frequency varies as the square of the wave number, instead of linearly, as it does for light waves.

SECTION III

WAVE GROUPS

We must now examine in somewhat greater detail the conception of a wave group. We shall consider first a quite general type of wave disturbance, in which the wave velocity, and therefore the wave length, vary with the frequency in an arbitrary way.

Suppose that two infinite plane wave trains, of the same amplitude and moving in the same direction, but with slightly differing frequencies, are superimposed on one another. Let us enquire what is the nature of the resulting disturbance. Let

ν, ν' be their frequencies, and N, N' their wave numbers. Then the resultant displacement of the two waves may be represented by

$$\sin 2\pi (\nu t + Nz) + \sin 2\pi (\nu' t + N' z).$$

Expressing this as a product we obtain

$$2 \sin 2\pi \left(\frac{\nu + \nu'}{2} t + \frac{N + N'}{2} z\right) \cos 2\pi \left(\frac{\nu - \nu'}{2} t + \frac{N - N'}{2} z\right).$$

The first factor represents a wave train of wave length approximately equal to $1/N$, the second a wave train of much greater wave length. The disturbance therefore consists of a succession of wave groups. The breadth (wave length) of each wave group is $1/(N - N')$. Thus the broader each wave group is, the nearer together are the wave lengths of the two wave trains that, superimposed on each other, make up the train of wave groups. The velocity with which each wave group travels is

$$\frac{\nu - \nu'}{N - N'}.$$

The two frequencies being very near together, this is approximately equal to $\frac{d\nu}{dN}$, the group velocity. It is noteworthy that for light waves, in free space, where ν is equal to cN, the two are exactly equal.

A succession of wave groups can be resolved into two plane waves; we must now consider the form of an isolated wave group. At any instant of time an isolated wave group can be represented by a wave function of the form* (cf. Fig. 4)

$$\psi = A(z)\, e^{2\pi i N_0 z} \qquad \ldots\ldots(7),$$

where $A(z)$ is a varying amplitude that falls to zero outside the region in which the disturbance is. N_0 is the wave number. It is convenient to represent $A(z)$ by the error function

$$A(z) = Ae^{-(z-z_0)^2/\sigma^2} \qquad \ldots\ldots(8).$$

* We have written the formulae in the complex form appropriate to de Broglie waves. For other waves, the real part must be understood.

We do not imply that all wave packets have this shape, but the error function is convenient to handle mathematically. The function ψ, then, represents a wave packet centred at the point z_0, and of length of order of magnitude σ. Of course, the wave packet represented by (7) and (8) has no such thing as an exact length; we mean that practically all of $\int_{-\infty}^{\infty} |\psi|^2 dz$ is contributed by a range of z of this order of magnitude. We shall always assume that the length of the wave packet is very much greater than the wave length, i.e. that

$$\sigma \gg 1/N_0.$$

If the waves are de Broglie waves, then the wave packet describes a cluster of electrons, each of velocity $N_0 h/m$, and of density, at the point z,

$$A^2 e^{-2(z-z_0)^2/\sigma^2}.$$

The wave function (7) can be analysed into its Fourier components by means of Fourier's integral theorem. We have, that, if ψ be any function*,

$$\psi = \int_{-\infty}^{\infty} C(N)\, e^{2\pi i N z}\, dN \qquad \ldots\ldots(9),$$

where

$$C(N) = 2\pi \int_{-\infty}^{\infty} \psi(z)\, e^{-2\pi i N z}\, dz \qquad \ldots\ldots(10).$$

If ψ is given by (7) and (8), then (10) reduces to

$$C(N) = \sqrt{\pi}\sigma A e^{-\pi^2\sigma^2(N_0-N)^2 + 2\pi i z_0 (N_0 - N)} \qquad \ldots\ldots(11).$$

It is instructive to verify the formula (9) in this case by direct integration.

It follows from (11), and is clear from other considerations, that the wave numbers of the plane waves of which a wave packet is built up all lie in a small range about the value N_0, and that the smaller the wave packet the broader is the range. If ΔN be the breadth of the range from which all the com-

* Cf. Whittaker and Watson, *Modern Analysis*, p. 188.

ponents that have appreciable amplitude come, and if σ be the breadth of the wave packet, then we see from (11) that

$$\sigma . \Delta N \sim 1 \qquad \ldots\ldots(12).$$

The sign $\sim$ denotes that the two quantities have the same order of magnitude.

As we have stated before, the wave group moves forward with the group velocity $\frac{d\nu}{dN}$, N being given the value N_0. For light waves the velocity with which the wave packet moves is exactly this. For other waves, in which the group velocity is itself a function of N, one cannot give a precise meaning to the velocity of the group, because the wave group spreads as it goes along. σ therefore increases as the wave group moves forward. An account of this spreading is given in any treatise on wave motion*, and we shall here assume its chief properties.

The rate at which the length of the wave group increases is equal to the difference in the group velocity, $\frac{d\nu}{dN}$, for the components of greatest and smallest wave number that make up the wave packet. This is equal to

$$\frac{d^2\nu}{dN^2} \Delta N \qquad \ldots\ldots(13).$$

The wave packets that we have described are as monochromatic as their size allows them to be. It is of course possible to form wave packets of non-monochromatic waves, such as would be formed if white light fell on an aperture that was opened and then closed. The relationship (12) may therefore be generalised; if we have a wave packet of length σ, and resolve it into its Fourier components, and if these Fourier components have wave numbers lying in a range ΔN, then $\sigma \Delta N$ *cannot be less than* unity.

The rate at which the wave packet spreads is still given by (13).

* A concise account has been given by Darwin, *Proc. Roy. Soc.* A, vol. CXVII, p. 258 (1927). See especially equations (4.4) and (4.5).

SECTION IV

THE UNCERTAINTY PRINCIPLE

Suppose that (7) represents a group of de Broglie waves. The wave group, having wave number N_0, should describe the behaviour of a cluster of electrons each moving with velocity v_0 equal to hN_0/m, such as might have been formed if a stream of electrons of this velocity had been fired at an aperture that was open for a short time only. The length of the wave packet is σ, so we must imagine the aperture open for a time σ/v_0. We have shown that the wave group as a whole moves forward with velocity equal to v_0, and so in this respect the wave group describes correctly the motion of the cluster of electrons. However, the wave group spreads. The rate of spreading is equal to $\frac{d^2\nu}{dN^2}\Delta N$; since ΔN is equal to $1/\sigma$, the rate of spreading is $\frac{d^2\nu}{dN^2}\Big/\sigma$, which, on performing the differentiation, reduces by equation (2), to

$$m/h\sigma.$$

It follows that the wave packet only describes the behaviour of electrons of the cluster of electrons correctly, if the electrons have not all got exactly the same velocity, but have velocities distributed about the value v_0, in a range of magnitude Δv, where

$$\Delta v = m/h\sigma.$$

The cluster of electrons would then spread, in the way that the wave packet does.

That the wave packet (7) represents a cluster of electrons with velocities distributed over a small range can be seen in another way. We assume always that $|\psi(x)|^2\,dx$ is the probability that an electron lies between x and $x + dx$. Further, a beam of waves of wave number N represents a stream of electrons of velocity hN/m. It is reasonable to assume, therefore, that if, as in equation (9), we resolve ψ into its Fourier components, then $|C(N)|^2\,dN$ is the probability that an electron in the cluster has velocity between hN/m and $h(N + dN)/m$. From (11) we

see that C (N) is only appreciable in a range of N of length $1/\sigma$. Therefore, electrons in the cluster have their velocities distributed in a range of order of magnitude $h/m\sigma$. If therefore the electrons have velocities distributed in a range of this order of magnitude, we can describe the behaviour of the cluster by a wave packet. If the velocities are distributed in a yet wider range, we can equally well represent the behaviour of the cluster by a wave packet, the waves being in this case non-monochromatic. If the range of velocities were smaller, then it would be impossible to represent the behaviour of the cluster by a wave packet.

If a stream of electrons, all with the same velocity, were to fall on an aperture and were allowed to pass through for a short time only, then it might happen that some of them would be disturbed by the opening and shutting of the shutter. Shutters are composed of atoms, and atoms are surrounded by electrostatic forces, and these might affect the velocity of the electrons. We have therefore two possibilities before us: either the behaviour of clusters of electrons cannot always be described by the wave mechanics; or it is impossible, in the nature of things, to construct a shutter device that will disturb the electrons so little that their velocities are distributed in a smaller range than that allowed by (12). We believe the latter to be the case. We shall return to this hypothesis in Section v.

SECTION V

WAVE DESCRIPTION OF A SINGLE ELECTRON

We have shown how the motion of a cluster of electrons may be described by the motion of a wave packet. Provided there is a certain lack of homogeneity in the velocities of the electrons, we can always find a wave function ψ, obeying the wave equation, such that $|\psi|^2$ will give the density of the electrons at any point and at any time. There is, however, one further point that we must investigate before we can be sure that the description of the phenomena by means of a wave packet is consistent with

experiment. Since $|\psi|^2$ gives the density of electrons, $\int |\psi|^2 d\tau$ over all space must be equal to the number of electrons in the cluster. Now if ψ is a solution of the wave equation, then $A\psi$ is also a solution, and so we can make $\int |\psi|^2 d\tau$ equal *initially* to any number that we please. The question is, will it stay constant? For if it does not, our theory predicts an increase in the number of electrons in the cluster, as the cluster moves along, which is altogether at variance with experience. It is, however, quite easy to prove that this integral is constant, i.e. that its time derivative is zero*. Our theory is therefore satisfactory in this respect.

We have stated that $|\psi|^2$ is equal to the density of electrons at any point. An equivalent statement is that $|\psi|^2 dx dy dz$ is equal to the probability that an electron is in the volume element $dx dy dz$. Looked at from this point of view, we can see how a wave packet can describe the motion of a single electron. Let us imagine that a very weak beam of electrons is falling on an aperture, and that the aperture is opened for so short a time that it is doubtful whether an electron will get through at all, and very unlikely that two will. Then a "region in which there may be an electron" passes through the aperture and out into space. The motion of this region may be represented by a wave packet, just as before; only now $\int |\psi|^2 dx dy dz$ represents, not the number of electrons in the cluster, but the probability that an electron has got through the aperture at all. If there is a 50 per cent. probability that an electron has got through, then the integral is equal to $\frac{1}{2}$; if we know that just one has got through, and no more, then

$$\int |\psi|^2 dx dy dz = 1.$$

What meaning can we now give to the spreading of the wave packet? We cannot say that some of the electrons have a velocity slightly greater than that of the original beam, and some slightly less, because there is only one electron. But when we

* Cf. Appendix, Note 4.

remember that the wave packet represents all the points where it is possible for the electron to be, it becomes clear what the meaning is. After passing the aperture, the velocity of the electron described by our wave packet is not known exactly; the wave packet tells us that the velocity *may* be rather greater or rather less than that of the original beam, so that the region in which the electron *may* be found becomes steadily wider. If the velocity of the electron is known exactly, then we cannot find a wave function ψ obeying the wave equation, and such that the probability that an electron will be found in the volume element $dxdydz$ is $|\psi|^2 dxdydz$. But if we suppose that the electron may have been disturbed by the opening and closing of the shutter, so that there is this uncertainty in its velocity, of order of magnitude not less than $h/m\sigma$, then we can find such a wave function, and the wave description gives essentially the same probability of the electron being found at any point as the Newtonian mechanics would, provided of course that there are no fields present that vary in a distance comparable with a wave length.

We have pictured the wave packet as being formed when a beam of electrons falls on an aperture that is open for a short time only. But if we are content to do without a picture of how the wave packet is formed, then the wave description may be applied to a much more general class of phenomena than this. Our aperture, and the beam of electrons falling on it, may be thought of as a device whereby we may determine the initial position and velocity of an electron, both with a certain degree of error. The behaviour of the wave packet tells us where the electron will go, in so far as this can be predicted from the inaccurate initial determination of its position and velocity. Now suppose that by any device whatever we measure the position and velocity of the electron. No measurement is absolutely accurate; suppose that we measure the position along the z-axis, and find it to be z_0, with a probable error σ. Then, if there were a wave packet of de Broglie waves, centred at z_0, and of length σ, the knowledge of the position and velocity of

the electron that this wave function would yield is just what we have obtained from our measurement. Suppose also that we measure the velocity of the electron, and find it to be v_0, with a probable error τ. Then our knowledge is just what could be deduced from the wave packet, if the wave numbers of its Fourier components lie in a range $m\tau/h$ about the value mv_0/h.

It is only a short step further to the point of view that regards a wave packet of de Broglie waves as simply a method of expressing the results of any experiment that could be made to discover the position and velocity of an electron. The wave function is, so to speak, just a convenient shorthand. The waves are not waves in any medium. There are no waves accompanying an electron, until we have observed the electron. Then we make use of the wave representation to embody the results of our observations. The wave equation tells us what may be deduced, from our observations, about the future position and velocity of an electron.

The result of an experiment cannot be represented by a wave function, if the experiment gives us too exact a knowledge of the position and velocity of the electron. We must have, in fact,

$$\sigma\tau > h/m.$$

At the present time we believe that it is fundamentally impossible to determine the position and velocity of an electron, at the same instant, with an accuracy greater than this. Our most compelling reason for believing this is that the wave description accords with the experimental facts, but it is further interesting that no known method of observing electrons could possibly give us an accuracy greater than this.

Suppose, for instance, we have an electron, and observe it at two instants of time, and wish to deduce from our observations its position and velocity. To observe the electron we must shine light on it, and unfortunately, each time we observe it the electron will scatter a quantum of light and will itself recoil. The recoil cannot be allowed for completely, and, as we shall now show, the more we find out about the position, the less we

know about the recoil, and therefore the less we can find out about the velocity.

Suppose we want to find the z-coordinate of the electron. We illuminate the electron with light from the direction OZ (Fig. 5),

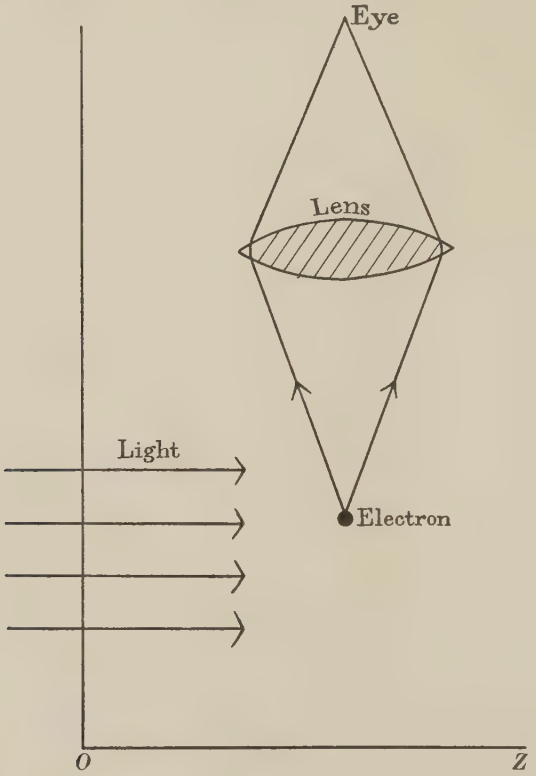


Fig. 5.

and hope to observe a scattered quantum. Momentum is conserved when a light quantum is scattered, so if a quantum is scattered through an angle θ, the electron acquires a certain momentum, of which the component along the z-axis is

$$\frac{h\nu}{c}(1 - \cos\theta), \quad \text{or} \quad \frac{h}{\lambda}(1 - \cos\theta),$$

where λ is the wave length of the light. This momentum would be known, and would not produce any uncertainty in the velocity, if the direction of the scattered light quantum could be determined. But in order to determine the position of the electron we must bring the light that it scatters to a focus by means of a lens. If we wish to determine the position accurately, we must use a lens of large aperture. The error Δr in the position of the electron due to the finite resolving power of the lens, will be of order of magnitude

$$\lambda f/R,$$

where f is the distance of the electron from the lens, and R is the radius of the aperture. Now the uncertainty in the direction in which the light quantum is scattered is $2R/f$. The uncertainty Δp in the z-component of the momentum, *after* the determination of the position, is of order of magnitude

$$\frac{h}{\lambda}\frac{R}{f}.$$

It follows that we cannot know the position and the momentum, at a given instant of time, with a greater accuracy than that given by

$$\Delta p \Delta r \sim h.$$

SECTION VI

Suppose that an astronomer wishes to predict the time of an eclipse; he will make measurements of the position of the moon at various times, from which he can deduce its velocity. Then, knowing the force on the moon due to the sun and the earth, he can work out the orbit of the moon, using the Newtonian mechanics, and so calculate when the moon will be between the earth and the sun. His original measurements will not be absolutely accurate, and there may be an uncertainty of a second or so in his predictions of when the eclipse will begin.

Now, the results of his original measurements may be represented by a wave function, which specifies the region in which

the moon may be. The motion of this region may be calculated from the wave equation for a particle of mass M, M being the mass of the moon. The path so calculated will be exactly the same as that calculated from the Newtonian mechanics, because the wave length, h/Mv, is enormously smaller than the distances involved. The wave equation will tell us, just as well as the Newtonian mechanics, when the eclipse will occur, in so far as it can be deduced from the original experiment.

The chief difference between the wave mechanics and the old mechanics is that, whereas the latter makes predictions by considering all the orbits that are consistent with the original measurements, the wave mechanics expresses only the results of the measurements. In considering the motion of the moon, the Newtonian mechanics gives the more natural representation, because by increasing the accuracy of our telescopes, we can get nearer and nearer to a measurement of real orbits. For electrons, where there is a limit to the accuracy of experiments, and the true orbits are in the nature of things unobservable, the wave mechanics gives the more natural representation. Moreover, when the two theories make different predictions, as they do when atomic fields are concerned, the predictions made by the wave mechanics are in accordance with experiment, so far as is known at the present time.

CHAPTER IV

THE THEORY OF STATIONARY STATES

SECTION I

An atom consists of a heavy nucleus and of a number of electrons. The simplest of the atoms is the hydrogen atom, in which there is only one electron. The electron is supposed to move somehow in the attractive field of the nucleus; a certain amount of work would be required to remove it, or, conversely, a certain amount of energy is released when the atom is formed. The atom therefore is a system possessing negative energy.

According to the Newtonian system of mechanics, a hydrogen atom could exist with any (negative) energy. For a possible orbit in which the electron could move is a circle round the nucleus, with radius r and velocity v, so long as the centrifugal force and the attractive force of the nucleus are in equilibrium with each other. This will be the case if

$$\epsilon^2/r^2 = mv^2/r,$$

i.e. if

$$r = \epsilon^2/mv^2 \qquad \ldots\ldots(1).$$

Now if E be the energy of the electron, equal to the sum of the kinetic energy and the potential energy, then E is given by

$$E = \tfrac{1}{2}mv^2 - \epsilon^2/r,$$

which, by virtue of (1), is equal to

$$E = -\tfrac{1}{2}mv^2.$$

Since v can have any value whatever, it follows that E can have any value less than zero.

Now this is contrary to experiment. The energy of an atom can only have one of certain definite series of values, E_1, E_2, E_3, ... For instance, in a hydrogen atom, the energy may only take the values

$$-K/n^2, \qquad n = 1, 2, 3, \ldots.$$

K is a constant equal to $2\pi^2 m\epsilon^4/h^2$. In particular, no hydrogen atom has ever been observed with less energy than $K/1^2$, and similarly every atom possesses a lowest energy E_1, below which the energy cannot sink.

The existence of these discrete energy levels can be shown by direct experiment. If electrons are fired into a monatomic gas, many of the scattered electrons are found to have given up energy to the gaseous atoms, but the amount of energy given up has always one of the values*

$$E_n - E_1,$$

or else is greater than $-E_1$. We conclude, therefore, that the atom originally had energy E_1, and that the bombarding electron, if it were to give the atom any energy at all, would have to give it enough to raise it to one of the other discrete values. It is not possible to do the experiment with hydrogen atoms, because hydrogen is not monatomic at ordinary temperatures; the values of the energy levels are known from spectroscopic evidence (cf. Chapter v), but there is no doubt that if the experiment could be performed with atomic hydrogen, the energy levels found would be those stated above.

An atom with energy E_n is said to be in its nth stationary state; an atom with energy E_1 in its normal state.

The Quantum Theory of Bohr is an expression of the fact that the energy of an electron in an atom can only have certain discrete values. If we assume that the electron in the atom does revolve in orbits, as the Newtonian mechanics demands, then the experiment that we have described shows that only certain of the mathematically possible orbits ever occur in Nature. In fact, only those occur for which

$$-\tfrac{1}{2}mv^2 = -K/n^2 \qquad \ldots\ldots(2).$$

Using the relation (1), that r is equal to ϵ^2/mv^2, we see that (2) is equivalent to

$$mrv = nh/2\pi;$$

* See, for example, Andrade, Chap. xii.

so that experiment shows that only those circular orbits are possible for which the angular momentum is a multiple of $h/2\pi$.

Now it is not known that the electrons do revolve in the orbits of the Newtonian mechanics. We have been able to account for the behaviour of beams of electrons in electrostatic fields by assuming that the beam behaves like a train of waves, and that the density of electrons at any point is given by the square of the amplitude of this beam. In the last chapter we have shown how to extend the wave description to the motion of a single electron; the square of the amplitude of the wave now gives the probability of the electron being at any point. In these descriptions there is no mention of the orbits of the electrons; therefore we abandon the attempt to describe the motion of an electron in an atom in terms of orbits, and attempt to obtain a purely wave description. We shall see that this wave description affords a means of determining the energy levels of any atom.

To introduce the reader to the new ideas involved, we shall discuss a familiar type of wave motion that we have not yet considered, namely, the vibrations of a piano wire.

SECTION II

NORMAL MODES OF A WIRE

A piano wire of given length l can emit, as well as its fundamental note, an infinite series of harmonics. If the nth harmonic is excited there will be $n - 1$ nodes spaced at equal intervals between the two ends of the wire; the wave length will therefore be given by the formula

$$\tfrac{1}{2}\lambda = l/n.$$

As was shown in Chapter II, the frequency ν of a vibration of wave length λ is given by

$$\nu = \frac{1}{\lambda}\sqrt{\frac{\rho}{T}},$$

where ρ is the mass per unit length, and T the tension.

Therefore, if the nth harmonic is excited, the frequency ν_n of the vibration is given by

$$\nu_n = \frac{n}{2l}\sqrt{\frac{\rho}{T}},$$

and the displacement y at time t of a point of the wire distant x from one end by

$$y = a \cos 2\pi (\nu t + \epsilon) \sin 2\pi (nx/2l) \qquad \ldots\ldots(3).$$

a, ϵ are an arbitrary amplitude and phase.

If the density of the wire is not uniform, the mode of vibration is not so simple, since the wave length varies along the wire. However, it is clear that a similar phenomenon occurs; there will be a definite series of frequencies,

$$\nu_1, \nu_2, \nu_3, \ldots$$

of which one, ν_1, will be the lowest. Corresponding to a frequency ν_n there will be a definite vibration, of arbitrary amplitude, and with $n - 1$ nodes between the ends of the wire, but differing somewhat from the sine curve considered before. If the wire is vibrating with frequency ν_n we can represent its displacement by

$$y = a \cos 2\pi (\nu_n t + \epsilon) \phi_n (x),$$

$\phi_n (x)$ being a function depending on the way in which the density varies in the wire, and, of course, vanishing at the two ends.

A wire vibrating with frequency ν_n is said to be vibrating in its *nth normal mode*. The normal mode with lowest frequency is called the lowest normal mode. The frequencies ν_n are called the characteristic frequencies of the wire (German "Eigenwerte" of the frequency).

The most general vibration possible to the wire is that in which all the normal modes are excited at once, each with arbitrary amplitude and phase. Then the displacement of any point of the wire will be

$$y = \sum_n a_n \cos 2\pi (\nu_n t + \epsilon_n) \phi_n (x),$$

where a_n, ϵ_n are arbitrary. If the density of the wire is uniform, ϕ_n is to be replaced by $\sin 2\pi nx/2l$.

SECTION III

NORMAL MODES OF A DE BROGLIE WAVE

Let us consider an electron shut up in a box. The walls of the box are to be of some perfectly elastic medium, so that the electrons are reflected without loss of energy. Now we have been able to describe all that we can observe of the behaviour of a free electron by means of a wave function ψ which obeys the wave equation; perhaps the same method will describe the behaviour of an electron in a box. Just what kind of solution to look for is not immediately obvious, so let us for a moment forget that our waves have any connection with electrons, and enquire as to what kind of oscillation waves in a box can perform.

In the first place, since the electron is always in the box, ψ must vanish outside the box. As we assumed in Chapter I, ψ must be continuous; and therefore ψ must vanish on the walls of the box. If now we confine ourselves to motion in one direction, say along the x-axis, we see that the wave length of the waves that ψ represents must, *just as in the case of the stretched string*, be a divisor of twice the length of the box. If l be the distance between the walls of the box, and λ the wave length of the waves, then

$$\lambda = 2l/n,$$

where n is an integer.

Now, for de Broglie waves just as for any other waves, to every wave length there corresponds a frequency. In the last chapter* we found that this frequency was

$$\nu = h/2m\lambda^2.$$

The de Broglie waves that describe an electron shut up in a box, therefore, are capable of vibrating only in a certain series of normal modes, with a definite series of frequencies, $\nu_1, \nu_2, \nu_3, \ldots$, where

$$\nu_n = hn^2/8ml^2 \qquad \ldots\ldots(4),$$

* Chap. III, equation (2).

The wave function, if the waves are vibrating in their nth normal mode, is

$$\psi_n = a e^{2\pi i \nu_n t} \sin 2\pi (nx/2l) \qquad \ldots\ldots(5).$$

a is here a complex constant, which includes the amplitude *and* the phase. That the time factor must be an exponential, and not the sine or cosine of equation (3), is seen if we substitute (5) in the wave equation (III. 6).

If there is an electrostatic field in the box, then again the wave function can vibrate in a series of normal modes, just as a stretched string of varying density can. The characteristic frequencies will then be given by some formula other than (4). The vibration in the nth normal mode will be described by a wave function

$$\psi_n = e^{2\pi i \nu_n t} \phi_n (x) \qquad \ldots\ldots(6),$$

where ϕ_n is some solution of the wave equation, vanishing at the walls of the box, and having $n - 1$ zeros between them.

We shall assume now that these wave functions describe the behaviour of an electron in a box. We have first to find a meaning for the arbitrary amplitude a of the wave function (5). In accordance with our usual assumption, we suppose that $|\psi(x)|^2 dx$ is the probability that the electron described by the wave function lies between x and $x + dx$. If then the wave function is to describe an experiment in which we know that there is just one electron in the box and no more, then the probability that the electron is somewhere in the box becomes a certainty, and so we must have

$$\int_0^l |\psi|^2 dx = 1.$$

This will determine the modulus of a. We find in fact that

$$|a| = \sqrt{(2/l)}.$$

The phase of a arbitrary.

In the same way, when there is a field in the box, and the normal modes are given by (6), we must choose the amplitudes of our vibrations so that

$$\int_0^l [\phi(x)]^2 dx = 1.$$

We found in the last chapter that a vibration of frequency ν describes the behaviour of an electron of energy $h\nu$. Therefore, if an electron in a box has energy equal to one of the particular values, $h\nu_n$, then its behaviour will be described by the wave function ψ_n. More exactly, if we *know* that an electron has energy $h\nu_n$, then the probability that its position lies between x and $x + dx$ is $|\psi_n(x)|^2\,dx$.

Now the surprising thing about this wave description is that the wave mechanics appears to provide no wave function to describe the behaviour of an electron if its energy is not equal to one of these characteristic energies, $h\nu_n$. From this fact we must conclude either that the wave mechanics is incompetent to describe, under all circumstances, the behaviour of an electron in a box, or that an electron in a box *can* only have one of these "characteristic energies." Only experiment can decide which of these two alternatives is the true one.

For a box of ordinary size, these characteristic energies lie very close together. (If the box is 1 cm. long, and the energy of the electron about 20 volts, the interval between successive energy levels is $3{\cdot}2 \times 10^{-7}$ volt.) To obtain a measurable interval between the energy levels, we must make our box very much smaller—of atomic dimensions in fact. Such a "box" is provided by the attractive force of the hydrogen nucleus that keeps an electron bound in a hydrogen atom. As we stated in Section 1, it is found experimentally that an electron bound in a hydrogen atom *can* only have certain discrete energies. So we begin to believe that the wave mechanics fits nature with exquisite economy; it only provides wave functions to describe electrons with such energies as electrons are found in nature to have.

It is not immediately obvious that an electron bound in a hydrogen atom will behave like an electron shut up in a box. However, there is very little difference between the two cases. Imagine a box, of which the walls are not rigid reflecting surfaces, but repulsive fields, which push the electron back when it tries to get out of the box. The potential energy of the

fields is shown in Fig. 6, by the upper full line. The vertical dotted lines show the point at which the electron is turned back.

Now we have already seen (Chapter II, Section III) how a train of waves, representing an electron of energy E, is reflected by a repulsive field. As V increases, the wave length gets longer

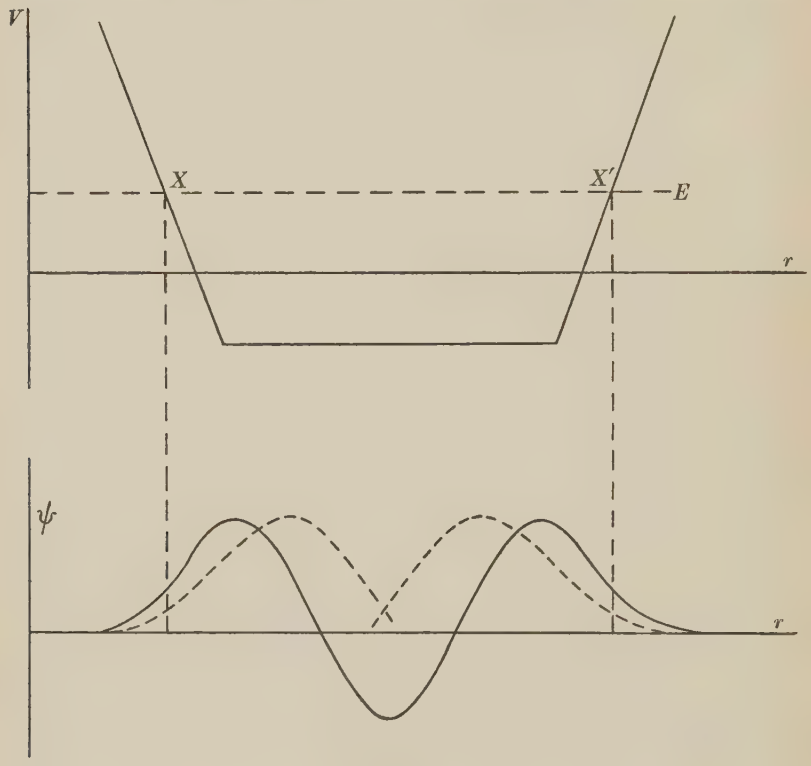


Fig. 6.

and longer, until we come to the point marked X or X' in Fig. 6, where the electron should be turned back. At this point the wave function begins to fall away exponentially, there being a kind of "total reflection" of the wave. Now for given E and given position of the reflecting field, the *phase* of the incident and reflected waves is determined. It is therefore clear that here

also it is only for certain values of E that we can obtain a standing wave reflected from both walls. For other values of E, if we try to construct the incident and reflected waves, starting from both ends, then they do not "fit" in the middle—as shown by the dotted line in the figure. The full line shows

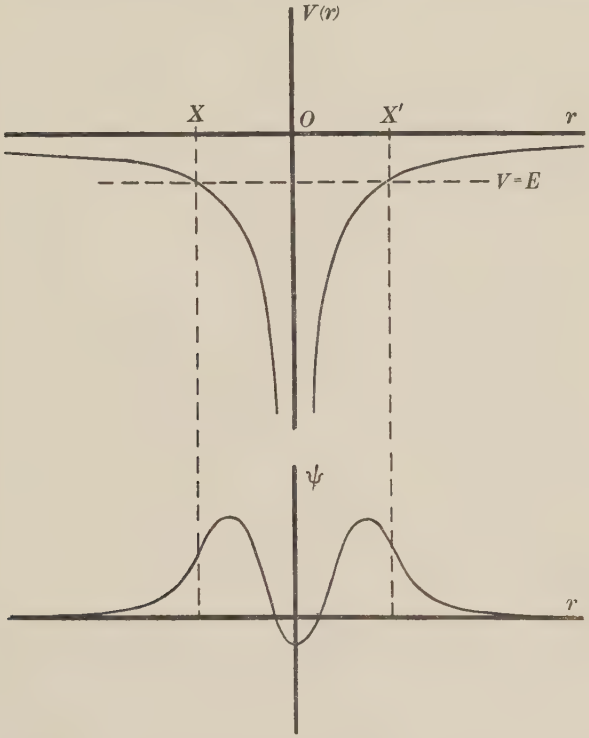


Fig. 7.

ψ in a normal mode, falling away outside the interval in which the classical electron would be.

Now, a hydrogen atom is simply an electron bound by an electrostatic force, which pulls it back if it tries to get away from the nucleus. The wave function therefore will vibrate in normal modes, and we shall only have wave functions describing the behaviour of electrons of certain discrete energies.

We shall show in Section VI that these energies are the actual energies of which a hydrogen atom is found experimentally to be capable.

The inverse square law field of the nucleus, and, below, the wave function ψ, are shown in Fig. 7. OX is here the distance ϵ^2/E, beyond which the classical electron cannot get. We can see qualitatively at what intervals the characteristic energies will occur. The lowest energy level will occur when XX', which is equal to $2\epsilon^2/E$, is about the same length as half the corresponding wave length, i.e. $\frac{1}{2}h/\sqrt{2mE}$. This gives an energy of $32\epsilon^4 m/h^2$, which is the right order of magnitude. It is further clear that as E approaches zero, the levels will be closer and closer together.

The electron in a hydrogen atom has three degrees of freedom; let us denote its position, relative to the nucleus, by $\mathbf{r}$. The wave function ψ, then, that describes the behaviour of the hydrogen atom, will be capable of vibrating in a certain series of normal modes, each with its characteristic frequency. The wave function describing the vibration in the nth normal mode will be of the form

$$\psi_n = e^{2\pi i \nu_n t} \phi_n(\mathbf{r}), \qquad n = 1, 2, \ldots .$$

The functions ϕ_n will be evaluated in Section VI. ψ_n, or ϕ_n, satisfies the wave equation

$$\nabla^2 \psi_n + \frac{8\pi^2 m}{h^2}(E_n - V)\psi_n = 0 \qquad \ldots\ldots(7),$$

where $E_n = h\nu_n$, and V is the potential of the electron in the field of the nucleus. The boundary condition satisfied by ψ is that ψ shall fall off exponentially for large r. $|\psi|^2\, dx\,dy\,dz$ is the probability that the electron lies in the volume element $dx\,dy\,dz$. The amplitude of the vibrations must therefore be chosen so that

$$\int |\psi|^2\, dx\,dy\,dz = 1.$$

The integration is now over all space, there being no definite walls to the atom; but since ψ falls off exponentially, very little will be contributed to the integral by distances greater than ϵ^2/E.

SECTION IV

THE ORTHOGONAL PROPERTY OF THE WAVE FUNCTIONS

Let us return to the idea of an electron moving in a box, in which there is no field. We found in Section III that if the electron has energy E then the wave function ψ must satisfy the equation

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 mE}{h^2}\psi,$$

and vanish at $x = 0$ and $x = l$, the walls of the box. We obtain a series of energies $E_1, E_2, E_3, \ldots$ for which this is possible, and a series of wave functions $\psi_1, \psi_2, \ldots$, where

$$\psi_n = a \sin(\pi n x/l) \qquad \ldots\ldots(8),$$

and, if there is just one electron in the box,

$$|a| = \sqrt{(2/l)}.$$

We may for convenience take a to be real. These wave functions satisfy the "normal" relation

$$\int_0^l |\psi_n|^2 \, dx = 1 \qquad \ldots\ldots(9.1),$$

and the "orthogonal" relation

$$\int_0^l \psi_n(x)\,\psi_{n'}(x)\,dx = 0, \quad n \neq n' \qquad \ldots\ldots(9.2).$$

As is well known*, any function $f(x)$ that vanishes at the boundaries can, in the interval $0 \leqslant x \leqslant l$, be expanded in a series of the functions, ψ_n, of the form

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \qquad \ldots\ldots(10).$$

The expansion is an ordinary Fourier expansion. The coefficients c_n are found by multiplying both sides of (10) by $\psi_n(x)$, and integrating from 0 to l. We obtain

$$c_n = \int_0^l f(x)\,\psi_n(x)\,dx \qquad \ldots\ldots(11).$$

* Cf. Whittaker and Watson, *Modern Analysis*, p. 165.

Now let us suppose that there is an electrostatic field in the box, in which the potential of the electron is $V(x)$. Then the wave function, corresponding to a characteristic energy E_n, will satisfy the equation

$$\frac{d^2\psi_n}{dx^2} + \frac{8\pi^2 m}{h^2}(E_n - V)\psi_n = 0 \qquad \ldots\ldots(12)$$

and vanish at $x = 0$ and $x = l$. We choose the amplitude of ψ_n so that (9.1) shall be true; it will now be shown that (9.2) is true also for these functions.

Multiply (12) by $\psi_{n'}$; then take the equation satisfied by $\psi_{n'}$ and multiply by ψ_n; subtract the two equations from each other. We obtain

$$\psi_{n'}\frac{d^2\psi_n}{dx^2} - \psi_n\frac{d^2\psi_{n'}}{dx^2} + (E_n - E_{n'})\frac{8\pi^2 m}{h^2}\psi_n\psi_{n'} = 0.$$

The left-hand term is equal to

$$\frac{d}{dx}\left[\psi_{n'}\frac{d\psi_n}{dx} - \psi_n\frac{d\psi_{n'}}{dx}\right].$$

Now ψ_n and $\psi_{n'}$ both vanish at 0 and l. If therefore we integrate from 0 to l we obtain

$$(E_n - E_{n'})\int_0^l \psi_n\psi_{n'}\,dx = 0.$$

Unless E_n and $E_{n'}$ are equal, (9.2) follows.

The series of functions $\psi_1, \psi_2, \ldots$ then, are very similar to the Fourier functions (8). We can expand* any function $f(x)$, given in the range 0 to l and vanishing at $x = 0$ and $x = l$, in a series of these functions of the form (10), the coefficient being given by (11).

(9.2) may be extended to the case when the range is infinite, and to the case of three dimensions. If, for instance, $\psi_n(\mathbf{r})$ and $\psi_{n'}(\mathbf{r})$ are wave functions of the hydrogen atom referring to different energies, we have

$$\iiint \psi_n(\mathbf{r})\,\psi_{n'}(\mathbf{r})\,dx\,dy\,dz = 0$$

* For a proof of this statement, see Courant-Hilbert, Chap. VI, p. 342.

over all space. Further, given any function $f(xyz)$, we can expand it in a series

$$f = \sum_1^\infty c_n \psi_n,$$

where

$$c_n = \iiint f \psi_n dx dy dz.$$

SECTION V

THE CONSERVATION OF ENERGY

It is difficult to believe that the energy of an electron shut up in a box is only capable of assuming one of a certain number of discrete values; what is there to prevent us from opening the lid of the box, and putting an electron in with any energy we like, and then shutting the lid? Let us examine, from a wave

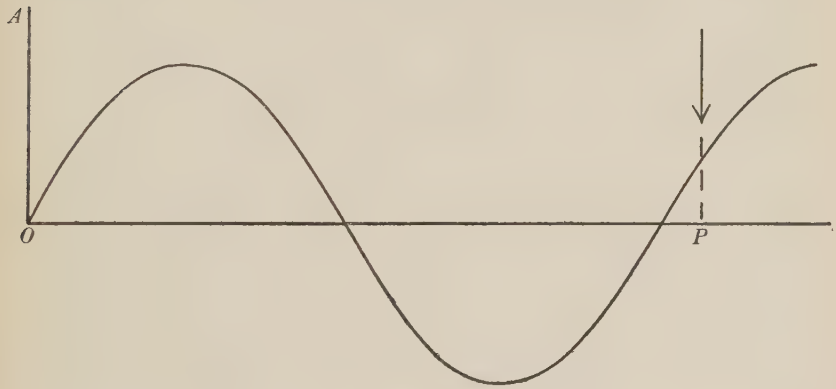


Fig. 8.

point of view, what will happen. We have first to insert the electron. Let us assume that a stream of electrons, of energy E, is being fired into the box, and is being reflected from the wall at O, which we shall take to be the point $x = 0$. Then the wave function describing the two streams of waves will, as in equation (II. 19), be

$$\psi = Ae^{2\pi i\nu t} \sin 2\pi Nx,$$

where

$$N = \sqrt{2mE}/h.$$

Now let us suppose that the lid is suddenly shut, at time t_0; in other words, let us suppose that an impassable barrier is suddenly erected at P, which we shall take to be the point $x = l$. What will happen to the waves? We can see from the analogy with waves in a stretched string. If one point, O, of a string is held fast, and waves are being reflected from it, and if another point P, not a node, is suddenly held, then, in the bounded piece of string OP, all the normal modes are excited. In the same way, for de Broglie waves, all the normal modes in the box will be excited. The vibrating wave function will then be, between $x = 0$ and $x = l$,

$$\psi = \Sigma c_n e^{2\pi i \nu_n t} \phi_n (x),$$

where* $\qquad \nu_n = n^2h^2/8ml^2, \qquad \phi_n = \sqrt{(2/l)} \sin \pi nx/l.$

To obtain the amplitude, c_n, we again refer to our analogy with the stretched string; the lid is brought down instantaneously, and we assume that ψ cannot alter instantaneously. Thus we must equate ψ directly after the lid is shut to the value that it had just before the lid was shut. That is to say, we must have

$$\Sigma c_n e^{2\pi i \nu_n t_0} \phi_n (x) = A e^{2\pi i \nu t_0} \sin 2\pi Nx \qquad \ldots\ldots(13).$$

The expression on the left is the Fourier expansion of that on the right. The coefficients c_n are obtained in the usual way; we obtain

$$c_n = e^{2\pi i (\nu - \nu_n) t_0} \int_0^l \sin 2\pi Nx \phi_n (x)\, dx.$$

We find, then, that in general, after the lid has been shut, that *all* the normal modes of which the de Broglie waves are capable have been excited at the same time. This can only mean that the electrons in the box have different energies. We assume that the number having energy $h\nu_n$ is given by $| c_n |^2$; or, if the intensity of the original beam is small, and only a few electrons

* It is convenient to introduce the "normalising constant" $\sqrt{(2/l)}$, since then

$$\int_0^l | \phi |^2 \, dx = 1.$$

are imprisoned in the box, then $|c_n|^2$ is the probability* that an electron has energy $h\nu_n$.

We see then that if we fire one electron with given energy into a box and shut the lid, the electron takes up one of the characteristic energies of the box—but we cannot foretell which. We know only the probability that it will take up any one of the characteristic energies. It appears therefore as though the wave mechanics predicted a violation of the conservation of energy.

But the difficulty is formal rather than real. Our perfectly reflecting walls are mathematical idealisations which have no counterpart in physics. Physically the nearest analogy is a repulsive electric field; the "lid" might be a negatively charged plate, which was suddenly brought up. Now to bring the plate up we shall have to do some work against the repulsive force of the electron. Quite clearly this can disturb the electron, and alter its energy. So the conservation of energy stands. After all, even in the Newtonian mechanics, in considering such abstractions as inextensible strings, we find instances where the conservation of energy breaks down, as, for instance, when a loose string is suddenly tightened. Actually the energy lost is taken up by vibration and heat motion in the string.

The ideas of the preceding paragraphs can be applied to a phenomenon that actually occurs in Nature. Let us consider the behaviour of the K electron in a heavy atom. This electron is, effectively, shut up in a "box," though the box will be of different size from that formed by the attractive force of the hydrogen nucleus. The wave function therefore that describes the electron will be able to vibrate in a series of normal modes. Let us suppose that the wave function is vibrating in the lowest of these, so that the electron is in its normal state in the K ring.

Now let us suppose that the nucleus of the atom is radio-

* When we speak of a probability p that something, A, will happen, we mean, simply, that if the experiment were repeated N times, N being large, A would happen pN times. Thus if $|a_n|^2$ be 1, it does not mean that one electron will have energy $h\nu_n$ *every* time the experiment is performed, but that if the experiment were repeated N times, the number of times an electron with energy $h\nu_n$ will be found is N.

active and that a β disintegration takes place. We may suppose that the β particle moves fast compared to the velocity of the K electron, so that the time that it takes to pass through the K ring is small compared to the natural frequency of the wave function. Let us neglect the chance of its hitting the K electron on its passage outwards. Then, to a first approximation, the only effect on the K electron will be to change the field in which it moves to that of a nucleus of charge $Z + 1$ instead of charge Z. That is to say, the electron moves in a "box" smaller than it did before. The wave function that described its state in the old box will no longer represent a normal mode in the new box; in the new box, all the normal modes will be excited. The electron, therefore, may have any of the energies possible to an electron in the field of a nucleus of charge $Z + 1$. There is no difficulty about the conservation of energy, because the departing β particle would have to pass through the field of the K electron, and could carry away any amount of its energy.

We shall now show how to calculate the probability that the electron is left in any given excited state. Let

$$\phi_1{}^z(\mathbf{r}), \quad \phi_2{}^z(\mathbf{r}), \ldots$$

be the series of wave functions for an electron in the field of a nucleus of charge Z. In the field of a nucleus of charge $Z + 1$ let the wave functions be

$$\phi_n{}^{z+1}(\mathbf{r}), \qquad n = 1, 2, 3.$$

Then, before the escape of the β particle, the wave function describing the state of the K electron is

$$\phi_1{}^z(\mathbf{r})\, e^{2\pi i \nu_1{}^z t} \qquad \ldots\ldots(14).$$

After the escape, the wave function will be

$$\sum_{n=1}^{\infty} c_n \phi_n{}^{z+1}(\mathbf{r})\, e^{2\pi i \nu_n{}^{z+1} t} \qquad \ldots\ldots(15).$$

To calculate the amplitudes c_n, we have to equate (14) and (15), at the moment at which the β disintegration takes place.

Let this be $t = 0$. Then we have

$$\sum_{n=1}^{\infty} c_n \phi_n{}^{z+1} = \phi_1{}^z.$$

Multiply by $\phi_n{}^{z+1}$, and integrate over all space. Then, by the normal orthogonal property of the wave functions, proved in Section IV, we have

$$c_n = \iiint \phi_n{}^{z+1} \phi_1{}^z \, dx\,dy\,dz.$$

This determines the coefficients c_n; the probability that the electron is left in the nth state is $| c_n |^2$.

SECTION VI

THE HYDROGEN ATOM

So far we have only discussed, explicitly, motion in one dimension. The electron in a hydrogen atom has, of course, three degrees of freedom. We shall therefore begin by discussing the behaviour of an electron shut up in a three-dimensional box. We shall imagine a rectangular box, the lengths of whose sides are l_1, l_2, l_3.

The wave function must vanish on the walls of the box; a possible normal mode is therefore

$$\psi = e^{2\pi i \nu t} \sin 2\pi n_1 x/2l_1 \sin 2\pi n_2 y/2l_2 \sin 2\pi n_3 z/2l_3,$$

where n_1, n_2, n_3 are any three whole numbers. It is not now so immediately obvious what the frequency is, there being no wave length; but if we substitute ψ into the wave equation (III. 6), and put $V = 0$, we obtain

$$\nu = \frac{h}{8m}\left(\frac{n_1{}^2}{l_1{}^2} + \frac{n_2{}^2}{l_2{}^2} + \frac{n_3{}^2}{l_3{}^2}\right).$$

A normal mode is therefore defined by three integers, n_1, n_2, n_3.

If to any given frequency there is more than one normal mode, the normal mode is said to be degenerate; e.g. if l_1 and l_2 are equal to each other, one will clearly obtain the same frequency

by interchanging the values of n_1, n_2, though this will give a different vibration.

The "box" in which the electron of a hydrogen atom is confined is not square but spherical, and it is convenient to use spherical polar coordinates (r, θ, ϕ). The wave equation must therefore be solved in spherical polar coordinates.

The equation, that the wave function vibrating with frequency ν must satisfy, is

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{\epsilon^2}{r}\right)\psi = 0 \qquad \text{.....(16),}$$

where $h\nu = E$, the energy of the electron that the wave function describes. We want to find a solution of this equation, that describes waves in the sphere for which $r < -\epsilon^2/E$, and that falls off exponentially for $r > -\epsilon^2/E$.

It is shown in any treatise on spherical harmonics* that a solution of such an equation as (16) is

$$\psi = e^{ik\phi} P_l^k(\cos\theta) f_l(r) \qquad \text{.....(17),}$$

if $f_l(r)$ satisfies the differential equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{df}{dr}\right) + \left[\frac{8\pi^2 m}{h^2}\left(E + \frac{\epsilon^2}{r}\right) - \frac{l(l+1)}{r^2}\right] f = 0 \text{.....(18).}$$

The functions $P_l^k(\cos\theta)$ are known as "Legendre" functions, and are defined by

$$P_l^k(\cos\theta) = \frac{1}{l!\,2^l}(\sin\theta)^{|k|}\frac{d^{l+|k|}}{d(\cos\theta)^{l+|k|}}\sin^{2l}\theta.$$

It will be seen that P_l^k, defined in this way, is equal to P_l^{-k}. k may have the values

$$-l, \quad -l+1, \quad 0, \ldots, \quad l-1, \quad l.$$

For all other values P_l^k vanishes. The first four functions are

$$\begin{aligned} P_0(\cos\theta) &= 1, \\ P_1(\cos\theta) &= \cos\theta, \\ P_1^1(\cos\theta) &= \sin\theta, \\ P_2(\cos\theta) &= \tfrac{1}{2}(3\cos^2\theta - 1), \\ &\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \end{aligned}$$

* Cf. Jeans, *Electricity and Magnetism*, Chap. VIII, p. 207, or Sommerfeld, *Wave Mechanics*, Chap. I, p. 8.

The function $e^{ik\phi}$ represents what we may call a "ϕ wave." As we describe a circle round the z-axis, ψ oscillates k times. If we drew a cylinder of radius ρ about the z-axis, there would be waves on the surface of the cylinder of wave length $2\pi\rho/k$. This corresponds to a momentum of $kh/2\pi\rho$, so if the electron is at distance ρ from the nucleus, the component of its momentum tangential to the cylinder and perpendicular to the z-axis is $kh/2\pi\rho$. The wave function (17) therefore describes an electron of angular momentum $kh/2\pi$ about the z-axis.

In the same way we can show that the total angular momentum is $lh/2\pi$, though this is less elementary and we shall not discuss it.

$f_l(r)$ must represent the "r waves," i.e. waves that travel outwards from the nucleus, are reflected at the surface of the atom, and which come back again. The physical meaning of the term $-l(l+1)/r^2$ is interesting. We have stated that the wave function (17) represents an electron with angular momentum $lh/2\pi$. There would therefore be a centrifugal force $l^2h^2/4\pi^2mr^3$ tending to pull the electron out of the atom. The potential of this force is $l^2h^2/8\pi^2mr^2$. This is what the term corresponds to. The model does not explain the occurrence of $l(l+1)$ instead of l^2.

Our problem, then, is to find a solution of (18) that falls off exponentially for large r. We might add that the solution must be everywhere finite, for a wave function ψ that becomes infinite somewhere clearly does not describe a wave.

Let us examine the nature of the solution in the neighbourhood of the origin. Put $f = r^s$, and substitute in (18), and, as we may near enough to the origin, neglect all but the terms of lowest order, namely, of order $s-2$. We obtain

$$l(l+1) = s(s+1).$$

It follows that $s = l$, or $-(l+1)$. Thus there are two independent solutions of the equation; one behaves like r^l at the origin and the other like r^{-l-1}. Quite clearly we must take the former, for the solution must be finite everywhere.

To solve the equation we make the following substitutions: put

$$f = r^l g.$$

Then the equation becomes

$$\frac{d^2g}{dr^2} + \frac{2(l+1)}{r}\frac{dg}{dr} + \frac{8\pi^2 m}{h^2}\left(E + \frac{\epsilon^2}{r}\right)g = 0.$$

Then put $$g = e^{-\lambda r}\, Z(r),$$

where $$\lambda^2 = -\frac{8\pi^2 m E}{h^2}.$$

Note that E is negative, and λ therefore real. The equation becomes

$$\frac{d^2Z}{dr^2} + \left[\frac{2(l+1)}{r} - 2\lambda\right]\frac{dZ}{dr} + \left[\frac{\alpha}{r} - \frac{2\lambda(l+1)}{r}\right]Z = 0 \ldots\ldots (19),$$

where $$\alpha = \frac{8\pi^2 m\epsilon^2}{h^2}.$$

This equation can be solved in series; if we put

$$Z(r) = \sum_{s=0}^{\infty} a_s r^s,$$

substitute in (15), and equate coefficients of each power ot r to zero, we obtain

$$a_{s+1}\{(s+1)(2l+s+2)\} = a_s\{2\lambda(s+l+1) - \alpha\} \ldots\ldots (20).$$

From this recurrence relation we can write down a_s for any s, and so Z; and therefore ψ is known.

We now want to know whether or not ψ thus found falls off exponentially for large r. We therefore examine the behaviour of Z for large r. Now, for sufficiently large r, the influence of the first few terms in the series will be negligible in comparison with the later terms. Now for terms very far on in the series, s is great compared to n and λ; and so, approximately,

$$a_{s+1} : a_s = 2\lambda : s.$$

Therefore, for sufficiently large s,

$$a_s = C(2\lambda)^s/s!$$

where C is some constant. Therefore, for very large r (when only large s matters)

$$Z(r) \sim Ce^{2\lambda r}.$$

It follows that f also increases exponentially, since

$$f = r^l e^{-\lambda r} Z(r).$$

Therefore, in general, the solution increases exponentially for large r.

There is one condition under which f will decrease, namely, if the series $\sum_s a_s r^s$ terminates, so that $Z(r)$ is merely a polynomial. Then the factor $e^{-\lambda r}$ will have the predominating effect, and f will fall off as it should. This will be so if for any s the coefficient of a_s in the recurrence relation (20) vanishes. This implies that, for some integer s, greater or equal to zero,

$$\frac{\alpha}{2\lambda} - (s + l + 1)$$

should vanish.

Now $\alpha/2\lambda$ is equal to $\frac{2\pi m}{h} \frac{\epsilon^2}{\sqrt{2mE}}$. The condition is, then, that there should be an integer s greater or equal to zero, such that

$$E = \frac{2\pi^2 m\epsilon^4}{h^2} \frac{1}{(l + s + 1)^2}.$$

This gives just the value of the energy levels that is in agreement with experiment, for $l + s + 1$ can have all integral values from unity to infinity.

It is usual to write

$$l + s + 1 = n \qquad \text{.....(21),}$$

and to call n the principal quantum number. The values of the energy are therefore

$$E = \frac{2\pi^2 m\epsilon^4}{h^2} \frac{1}{n^2}.$$

If n is equal to unity, we have, from (21), that $l = 0$, and the wave function is seen to be

$$\psi = e^{2\pi i\nu t} \frac{1}{\pi a^3} e^{-r/a},$$

where $a = h^2/4\pi^2 m\epsilon^2$, which is equal to the radius of the first circular orbit in Bohr's theory. The factor $1/\pi a^3$ is inserted so that we may have

$$\int |\psi|^2 \, dxdydz = 1,$$

as will be the case if there is one electron in the atom.

If however $n = 2$, the stationary state is "degenerate"; corresponding to the one energy value, there are four possible wave functions; for we can have, from (21), $l = 0$ or 1. In the former case, k must be zero; in the latter case, it can have the values -1, 0, $+1$. The wave functions are

$$\psi = \frac{1}{2\sqrt{2\pi a^3}} e^{-r/2a}\left(\frac{r}{2a} - 1\right), \qquad n = 2, l = 0, k = 0,$$

$$\psi = \frac{1}{2\sqrt{2\pi a^3}} e^{-r/2a} \frac{r}{2a} P,$$

where

$$P = \cos\theta, \qquad n = 2, l = 1, k = 0,$$
$$P = \tfrac{1}{2}\sin\theta e^{i\phi}, \qquad n = 2, l = 1, k = 1,$$
$$P = \tfrac{1}{2}\sin\theta e^{-i\phi}, \qquad n = 2, l = 1, k = -1.$$

The multiplying factors are again chosen so that each wave function shall describe one electron in the atom.

The quantum l plays the rôle of the "azimuthal quantum number" in Bohr's theory. An electron with l equal to zero is in a state that was described in Bohr's theory by an n_1 orbit, that is to say, in an elliptic orbit of the maximum possible eccentricity. The charge distribution given by our wave function is spherically symmetrical! The essential feature of the elliptic orbit was, however, that it should penetrate nearer to the nucleus than the circular orbit, and this feature is retained by the wave mechanics, for the wave function for $l = 0$ remains finite at the origin, whereas the wave function for $l = 1$ vanishes at the origin. There is therefore a greater probability that an electron should be near the nucleus, if it is in a state for which $l = 0$, than if it is in a state for which $l = 1$.

In a more complicated atom, electrons for which $n = 1$ are called K electrons, those for which $n = 2$ are called L electrons, and so on. Electrons for which $l = 0$ are called S electrons, those for which $l = 1$ are called P electrons, and so on.

The total angular momentum is $lh/2\pi$; the angular momentum about the z-axis is $kh/2\pi$. k is sometimes called the "magnetic" quantum number.

It is particularly to be noted that, in the normal state, ψ is spherically symmetrical, and the theory therefore predicts zero angular momentum, in contradiction with Bohr's theory. In the last chapter we shall show that the atom has actually *half* a quantum of angular momentum, due to the "spin" of the electron.

SECTION VII

THEORY OF RADIOACTIVITY

The emission of α and β particles by a radioactive nucleus was a phenomenon that the classical mechanics could not account for in any natural way. We have to explain the fact that a particle should remain in the nucleus for a period enormously long compared to the frequencies that obtain inside the atom, and then, for no apparent reason, should be shot out with a velocity approaching that of light. No outside influence can be shown to influence the rate of radioactive decay; the cause of the disintegration must therefore lie inside the nucleus itself.

The nuclei of a given radioactive element emit α particles all of the same velocities, or at the most with two or three discrete velocities. The velocities of the β particles, on the other hand, form a continuous spectrum. It may be said at once that no convincing explanation has been given of the β disintegration. We shall confine ourselves to a discussion of the emission of α particles, which has been fully explained by the work of Gamow, and independently by Gurney and Condon in America.

Our fundamental assumption is that our knowledge of the position and velocity of any particle can be represented by a wave. We shall first show what wave will represent the facts of

radioactive disintegration, and then enquire what field of force will produce such a wave.

Let then ψ be the wave function that describes the position and velocity of an α particle. At any moment of time, the probability that the particle is in the nucleus is very much greater than that it will be in an equal volume outside; therefore the amplitude of the wave function in the nucleus must be very much greater than that of the wave function outside. If the particle is outside the nucleus, then it may be moving in any direction away from the nucleus, and it will move with a definite velocity v. These facts are described by a spherical wave diverging from the nucleus, of wave length h/mv. The energy of the α particle, both before and after the disintegration, will be equal to the kinetic energy of the particle in free space. Therefore the frequency of the waves is equal to $\frac{1}{2}mv^2/h$. Further, the probability that the particle should be in the nucleus becomes steadily smaller and smaller as the time increases. The amplitude therefore of the wave function in the nucleus becomes steadily less and less.

Now let us enquire into the nature of the field in the neighbourhood of the nucleus, in which the α particle moves. At large distances we know that there is a repulsive electrostatic force, due to the charge on the nucleus. The potential of the particle in this field will be $ZZ'\epsilon^2/r$, where Z is the charge on the nucleus and Z' the charge of the α particle. At small distances from the nucleus, however, this field must change into an attractive field of some kind which will enable the particle to remain there. Let us assume, therefore, that the potential energy of an α particle, plotted against the distance, is somewhat as shown in Fig. 9. For r greater than a given distance r_0 the field is repulsive; for smaller r it becomes attractive. We can deduce the chief features of radioactive decay without enquiring into the cause of this attractive force; but it may be a kind of surface tension that prevents the α particle from leaving the nucleus*. Now let E be the energy of the α particle. E is shown in the

* Cf. Gamow, *Proc. Roy. Soc.* vol. CXXVI, p. 632.

figure by the line PAB. Then, according to the classical theory, at the distances PA and PB, the particle would have zero kinetic energy. If placed at distance PB from the centre of the nucleus, it would fly away from the nucleus; if placed at distance PA, it would oscillate between the lines Aa, $A'a'$. It will not be possible for the particle to be between the lines Aa, Bb, where the kinetic energy is negative. According to the classical theory, therefore, if the particle is initially inside the nucleus, it cannot get out.

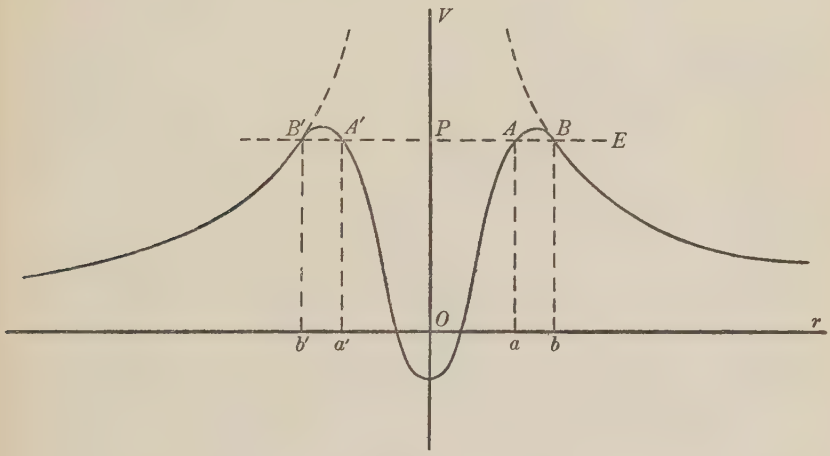


Fig. 9.

According to the wave mechanics, however, the behaviour of the particle will be determined by the behaviour of a wave function of wave length at each point $h/\sqrt{2m(E-V)}$. Between the lines Aa and Bb the wave length becomes imaginary; in other words, the wave suffers total reflection at the walls of the nucleus. It can vibrate, therefore, only in one of a series of normal modes, with definite frequencies. Thus the α particle in the nucleus, just like the electron in the atom, must have one of a series of discrete energies.

The amplitude of the wave, which is reflected at Aa, does not vanish at that point, but begins to fall off exponentially.

By the time we get to Bb the wave amplitude will have become very small, but not zero. The wave length now becomes real again, and so a wave of very small amplitude leaks out of the nucleus. When we get right outside the field of the nucleus there will be a spherical wave of very small amplitude, and of wave length $h/\sqrt{2mE}$.

Now since we have a wave leaking out of the nucleus, the amplitude of the wave vibrating in the nucleus must slowly die away. This appears clear from the analogy that we have drawn between these waves and other waves. In most other waves the amplitude determines the energy in the wave, and if energy is flowing away the amplitude must die down. It is moreover proved by Appendix Note 4.

Thus, if we have a wave inside the nucleus, representing a particle with positive energy E, the wave leaks out, and the amplitude of the vibrations inside the nucleus dies away. This, as we have seen, indicates a chance that the α particle has escaped.

To find the decay constant, we must start with a solution of the wave equation that vanishes outside the nucleus, and inside represents a vibration of frequency E/h, and unit amplitude*. A small wave will instantly leak through the potential barrier and spread outwards. The time required, perhaps of the order of years, for the amplitude of the wave in the nucleus to become appreciably smaller will be enormously greater than the period of these waves, so to all intents and purposes we have, after a short interval, a steady wave flowing away from the nucleus and a wave, of unit amplitude, in the nucleus. Now, if a/r be the amplitude of the wave that flows out of the nucleus, then the probability that an α particle crosses an element of area dS, at a distance r from the nucleus in time dt is $(a/r)^2\, dS.dt.v$, where v is the velocity of the α particles. The probability that it passes a sphere surrounding the nucleus is $4\pi^2a^2dt.v$. This is the probability that a disintegration takes place in time dt (if

* By unit amplitude is meant an amplitude such that

$$\iiint |\psi|^2\, dxdydz = 1.$$

the particle is certainly in the nucleus to begin with). The decay constant is therefore equal to

$$4\pi^2 a^2 v.$$

Gamow* has been able, without making precise assumptions about the form of the attractive field, to account for the Geiger-Nuttall law, which connects the decay constant of the various radioactive transformations with the velocity of the α particles emitted. This law states that if v is the velocity of the particle emitted, and κ is the decay constant, then

$$\log \kappa = A + B \log v.$$

A and B are constants; B has the same value for all three radioactive families; A has different values for the uranium, actinium, and thorium families.

ARTIFICIAL DISINTEGRATION

It is known that only certain of the lighter elements can be disintegrated on being bombarded by α particles, a proton being expelled. Gamow† assumes that in the lighter elements also there is such a potential barrier as illustrated in Fig. 8. Further, that an α particle can only cause disintegration if it surmounts this barrier, and gets into the nucleus. Suppose then a stream of α particles is fired at the nucleus. The stream is represented by a wave train. Let E now be the energy of each particle. Then as we go from B to A the wave function falls off exponentially. There will still be some amplitude remaining inside the nucleus, representing a finite probability that the α particle gets in. The probability is clearly greater for light nuclei, for then the thickness of the potential barrier is less. From these considerations, Gamow has been able to account for the observed variation of the number of disintegrations with the velocity of the particles, though, of course, this simple theory cannot account for the fact that nuclei of atomic number $4N$ are not disrupted at all. Neither does it show us why an α particle, once inside a nucleus, should expel a proton.

* Gamow and Houtermanns, *Z. Physik*, vol. LII, p. 496.

† Gamow, *Z. Physik*, vol. LII, p. 510.

CHAPTER V

THE ABSORPTION OF RADIATION

SECTION I

Suppose that we have a simple harmonic oscillator, such as a spring, that vibrates up and down with frequency ν_0; the equation of motion of the bob of the spring is then

$$\ddot{y} + 4\pi^2\nu_0^2 y = 0.$$

Now suppose that the bob is subject to a periodic force, of frequency ν, that gives it, in addition to the acceleration $-4\pi^2\nu_0^2 y$ due to the extension of the string, a further acceleration $a \sin 2\pi\nu t$. The equation of motion is then

$$\ddot{y} + 4\pi^2\nu_0^2 y = a \sin 2\pi\nu t.$$

The solution is

$$y = A \cos 2\pi\nu_0 t + B \sin 2\pi\nu_0 t + C \sin 2\pi\nu t,$$

where A and B are arbitrary, and

$$C = a/4\pi^2 (\nu_0^2 - \nu^2).$$

The spring, therefore, can vibrate in any way that was possible to it when it was free, with the "forced oscillations" $C \sin 2\pi\nu t$ superimposed.

The solution fails if $\nu = \nu_0$; that is to say, if the period of the external force is equal to that of the free spring. The two frequencies are then said to be in resonance. In this case the solution is

$$y = A \cos 2\pi\nu_0 t + B \sin 2\pi\nu_0 t + Dt \cos 2\pi\nu t,$$

where

$$D = a/4\pi\nu.$$

The spring vibrates with ever-increasing amplitude. The amplitude increases with the time, and therefore the energy increases with the square of the time.

Another example of a similar phenomenon is provided by the vibrations of a stretched piano wire. If a sound wave of frequency equal to one of its characteristic frequencies falls on the wire, the wire will vibrate with ever-increasing amplitude until a point is reached at which it gives off as much energy, in the form of sound waves, as it receives. If the frequency of the sound wave is not in resonance with one of the characteristic frequencies of the wire, then only very small forced vibrations are set up.

Now let us consider a hydrogen atom upon which light is falling. The behaviour of the electron in the atom is, as we know, determined by the behaviour of a wave, that can vibrate with one of a series of characteristic frequencies $\nu_0, \nu_1, \nu_2, \nu_3, \ldots$. The light, if monochromatic, consists of a periodic electromagnetic force. We shall therefore expect some resonance phenomenon to occur if the light is in resonance with one of the characteristic frequencies of the atom. However, the matter is not so simple as in our previous example, in which a wire vibrated under the influence of a sound wave, for the light does not act directly on whatever is vibrating in the de Broglie wave; it causes, rather, a periodic fluctuation in the refractive index. We shall see that the effect of this is not to increase the amplitude of the wave, but to change its frequency. It would, of course, be unsatisfactory if the theory predicted an increase of amplitude, for the amplitude tells us the total number of electrons present, which must remain a constant.

The refractive index of de Broglie waves at any point is $\sqrt{E/(E-V)}$, where E is the energy of the electron, and V its potential energy in any field that may be present. The light wave, a rapidly varying electric force, causes V to vary rapidly. We shall neglect the effect of the magnetic force. We shall show in the next section that the resonance effect is as follows. If the frequency of the light wave is the same as one of the characteristic frequencies of the atom, nothing in particular happens; only very small forced oscillations are set up. But if

the wave function ψ of the atom is already vibrating in one of its normal modes, of frequency, say ν_n, and if the frequency ν of the light is equal to the difference between ν_n and any *other* characteristic frequency ν_l of the atom, then the amplitude of the nth normal mode will slowly die down, and that of the lth be excited in its stead. All through the process $\int\int\int |\psi|^2 \, dx\,dy\,dz$ remains constant and so the wave mechanics does not predict the creation of any electrons.

An analogy with the stretched string will make clearer what is happening. We shall suppose that the string is not of uniform density ρ all the way along, so that the series of characteristic frequencies do not form an arithmetical progression. Now the wave velocity (which varies with the refractive index) is equal to $\sqrt{\frac{T}{\rho}}$, where T is the tension. So to alter the refractive index periodically, we have to alter T periodically, as we could by tying one end of the string to a vibrating support. Now let $\nu_0, \nu_1, \nu_2, \ldots$ be the characteristic frequencies of the string. If initially it is vibrating with frequency ν_n, then, if ν is equal to $|\nu_n - \nu_l|$, ν_l being any other characteristic frequency, the effect of the varying tension is to excite the lth normal mode, while the nth dies away. No energy will be lost by the string, since the pull that alters T is always perpendicular to the displacement. A proof that a string will behave in this way may be given on the lines of the proof for a wave function, given in the next section.

Suppose then we have an atom in its lowest stationary state of energy E_0. The wave function ψ vibrates with frequency ν_0, equal to E_0/h. Light of frequency ν falls on it; only oscillations of very small amplitude are set up, *unless*

$$\nu = \nu_0 - \nu_n = (E_0 - E_n)/h,$$

E_n being the energy of any one of the excited states. In this case the amplitude of the nth normal mode grows, and that of the first normal mode dies away. *This means that there is a*

probability, that increases with the time, that the atom has "jumped" to the nth excited state.

SECTION II

In this section we shall show that the wave functions that describe a hydrogen atom do in fact behave as we have stated that they do, and probabilities will be found for the excitation of the atom.

Let us take a plane polarised light wave, travelling along the z-axis, and with its electric vector in the zx plane. The wave length of ordinary light is of the order of magnitude 10^{-5} cm.; the dimensions of a hydrogen atom, 10^{-8} cm. Therefore, at any instant of time, the force on the electron is effectively the same at all points within the atom. The components of electric force within the atom are therefore given by

$$E_x = a \sin 2\pi\nu t, \qquad E_y = 0, \qquad E_z = 0.$$

Owing to the assumption that we have made, that the wave length is much greater than the radius of the atom, we shall not be able to apply our results to hard X-rays, and our analysis will not predict the Compton effect.

We neglect the influence of the magnetic force in the light waves.

The potential energy U of the electron in the field of the light wave will then be

$$U\,(xyz) = -\epsilon a x \sin 2\pi\nu t.$$

The wave equation, therefore, obeyed by the wave function ψ that determines the behaviour of the electron in the atom is

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2\psi - (V + U)\,\psi \qquad \text{.....(1),}$$

where

$$V = -\epsilon^2/r.$$

That ψ, obeying this equation, really does describe the behaviour of the electron, is a new assumption. We have so far only assumed that the equation is correct for fields that do not

vary with the time. It is, however, a not unreasonable generalisation to assume that it is also correct for rapidly varying fields.

To solve equation (1), we must remember that U, the potential energy of the electron in the field of the light wave, is very much smaller than V. ψ, then, will be only slightly different from what it would be if there were no light wave. We may write therefore

$$\psi = \psi^{(0)} + \psi^{(1)},$$

where $\psi^{(0)}$ satisfies the equation (1) with U set equal to zero, and $\psi^{(1)}$ is the small change in ψ caused by the presence of the light wave. If we substitute this value of ψ into (1), and neglect, as we may, terms in which a product of U and $\psi^{(1)}$ occurs, we obtain

$$\left[-\frac{ih}{2\pi}\frac{\partial}{\partial t} + \frac{h^2}{8\pi^2 m}\nabla^2 - V\right]\psi^{(1)} - U\psi^{(0)} = 0 \quad \ldots\ldots(2).$$

Now let us suppose that initially, at time $t = 0$, the atom is in its normal state. Then $\psi^{(0)}$ will represent the wave function vibrating in its lowest normal mode, and so, if $\phi_0, \phi_1, \phi_2, \ldots$ are the series of characteristic functions of the atom, we have

$$\psi^{(0)} = \phi_0(\mathbf{r})\, e^{2\pi i \nu_0 t}.$$

To find $\psi^{(1)}$, we expand it in a series of wave functions of the form

$$\psi^{(1)} = \sum_n C_n(t)\, \phi_n(\mathbf{r})\, e^{2\pi i \nu_n t} \qquad \ldots\ldots(3).$$

As shown in Chapter IV, any function of r and t can be expanded in this form, the functions behaving similarly to the Fourier coefficients

$$\sin r, \sin 2r, \sin 3r, \ldots.$$

The factors $e^{2\pi i \nu_n t}$ could be included in the coefficients $C_n(t)$, but it is more convenient to write the expression in the form (3).

Substituting (3) into (2) we obtain

$$\sum_n \frac{ih}{2\pi}\left\{\frac{d}{dt}C_n(t)\right\}\phi_n(\mathbf{r})\, e^{2\pi i \nu_n t} + U\phi_0(\mathbf{r})\, e^{2\pi i \nu_0 t} = 0.$$

Now from this equation we can find the coefficients $C_n(t)$. If we multiply both sides of the equation by $\phi_l(\mathbf{r})$, and integrate over all $\mathbf{r}$, then, remembering that

$$\iiint \phi_n(\mathbf{r})\,\phi_l(\mathbf{r})\,dxdydz = 0, \qquad n \neq l,$$

we have

$$\frac{ih}{2\pi}\left\{\frac{d}{dt}C_n(t)\right\}e^{2\pi i\nu_n t} + \iiint U\phi_0(\mathbf{r})\,\phi_n(\mathbf{r})\,dxdydz\,e^{2\pi i\nu_0 t} = 0.$$

Now we put in the value of U, namely,

$$U = -\epsilon a x \sin 2\pi\nu t.$$

If then we write

$$\iiint \epsilon x\phi_0\phi_n dxdydz = P_n,$$

the equation reduces to

$$\frac{ih}{2\pi}\frac{dC_n}{dt} = aP_n \sin 2\pi\nu t\, e^{2\pi i\overline{\nu_0-\nu_n}t}.$$

This equation can be integrated; an arbitrary constant appears in the solution. We choose this constant so that C_n shall be zero at time $t = 0$, because we have assumed that at this time the atom was known to be in the normal state, and so the wave function describing it is $\psi^{(0)}$. Therefore

$$\frac{ih}{2\pi}C_n(t) = \frac{1}{2i}aP_n\left[\frac{e^{2\pi i(\nu_0-\nu_n+\nu)t}-1}{2\pi i(\nu_0-\nu_n+\nu)} - \frac{e^{2\pi i(\nu_0-\nu_n-\nu)t}-1}{2\pi i(\nu_0-\nu_n-\nu)}\right] \qquad \ldots\ldots(4).$$

If we now refer to (3), we see that $\psi^{(1)}$, the forced oscillation set up by a light wave of frequency ν falling on the atom in its normal state, consists of vibrations of frequency $\nu_0 - \nu$ and $\nu_0 + \nu$ and ν_0, ν_1, ν_2, ..., all the characteristic frequencies of the atom. There is no resonance, that is to say, the amplitude of the forced oscillations do not increase, unless one of the denominators in (4) vanishes. This will only be the case if the frequency of the light is equal to the difference between ν_0 and one of the other characteristic frequencies of the atom.

If ν is equal to $\nu_0 - \nu_n$, then

$$\frac{ih}{2\pi} C_n(t) = \frac{1}{2i} aP_n t.$$

The amplitude of the vibration in the nth normal mode increases therefore with the time. The square of this amplitude, $| C_n(t) |^2$, should give the probability that, at any moment, the atom has jumped, under the influence of radiation, into the nth stationary state. Now

$$| C_n(t) |^2 = \frac{\pi^2 a^2}{h^2} | P_n |^2 t^2,$$

which increases as the square of the time. This is contrary to all experience; the probability must increase linearly with the time. In other words, the number of atoms that have jumped into the nth stationary state must increase linearly with the time.

The key to the paradox is that no light is ever strictly monochromatic; we must assume that the light has its energy distributed in a certain range of frequencies, having energy $I_\nu \, d\nu$ between the frequencies ν and $\nu + d\nu$. $| C_n(t) |^2$ will still give the probability that light of a given frequency has excited the atom. The probability that the atom has been excited by light with its energy distributed over a continuous frequency range is obtained by averaging over all ν in the range. If the frequency range includes the frequency $\nu_n - \nu_0$, then we shall find that the probability of excitation increases linearly with the time, as it should. Otherwise, it will remain very small.

We have

$$| C_n(t) |^2 = \frac{\pi^2 a^2}{h^2} | P_n |^2 \frac{2\{1 - \cos 2\pi(\nu_0 - \nu_n + \nu) t\}}{4\pi^2 (\nu_0 - \nu_n + \nu)^2}.$$

The energy per unit volume in a light wave, of which the amplitude of the electric vector is a, is $a^2/4\pi$. Therefore the probability that the atom is excited by the light of the whole frequency range is, in time t,

$$\frac{8\pi}{h^2} | P_n |^2 \int_0^\infty I_\nu \frac{1 - \cos 2\pi(\nu_0 - \nu_n + \nu) t}{(\nu_0 - \nu_n + \nu)^2} \, d\nu.$$

If we make the substitution

$$(\nu_0 - \nu_n + \nu)\, t = z,$$

this reduces to

$$\frac{8\pi}{h^2} \mid P_n \mid^2 t \int_0^\infty I_\nu \frac{1 - \cos 2\pi z}{z^2}\, dz,$$

where

$$\nu = \nu_n - \nu_0 + z/t.$$

For t large compared to the periods of the wave function, this reduces to

$$\frac{8\pi}{h^2} \mid P_n \mid^2 t I_{\nu_n - \nu_0} \int_0^\infty \frac{1 - \cos 2\pi z}{z^2}\, dz.$$

The integral can be evaluated, and is equal to $\frac{1}{4}$. Thus the probability, per unit time, that the atom is excited by light of energy density I_ν per unit frequency range, is

$$\frac{2\pi}{h^2} \mid P_n \mid^2 I_{\nu_n - \nu_0}.$$

The quantity P_n is known as the "matrix element" of the polarisation of the atom. We have assumed throughout that the atom was initially in its normal state; this is, of course, unnecessary. Suppose that the atom is initially in a state specified by the quantum numbers n, l, k, and we require the probability that the atom should "jump" into the state specified by the quantum numbers n', l', k'. The matrix element that gives the probability will be*

$$\iiint f_{ln}(r)\, P_l^k(\cos\theta)\, e^{\pm ik\phi} \begin{matrix} x \\ y \\ z \end{matrix} f_{l'n'}(r)\, P_{l'}^{k'}(\cos\theta)\, e^{\pm ik'\phi}\, dx\,dy\,dz \qquad \ldots\ldots(5),$$

where $f_{ln}(r)$ are the functions defined in Chapter IV, equations (17), (18), etc.

Now the lines corresponding to certain transitions are never found in nature; only lines are found for which $k - k' = 0$, or ± 1, and $l - l' = \pm 1$. This is known as the selection rule. It

* x, y, or z must be taken, according to the direction of the polarisation of the light.

can be seen that the matrix element (5) vanishes for such transitions as do not obey this rule; for z, y, and x may be expressed as $r\cos\theta$, $r\sin\theta\cos\phi$, etc., and it can be shown* that if the integration be carried over θ, ϕ, the integral vanishes unless l, l' differ by unity, and k, k', by unity or zero.

The theory that we have developed to account for the excitation of an atom does not take account of the corpuscular properties of light. So far as its action on an electron is concerned, the light is treated as an oscillating electric force, and we obtain the probabilities that under its influence the atom has jumped from one state to another. But, in a complete description of the phenomena, we must consider that the energy of the light is carried along in the form of quanta, and that now and then an atom is excited, and a quantum absorbed. That the probability of these excitations has to be calculated by the method that we have given, that makes no mention of light quanta, is a fault in the completeness of the theory. A more satisfying theory, in which light is considered as a stream of quanta, has been given by Dirac†; this theory will not be considered here. It leads to the same probabilities of excitation as we have obtained.

The theory is also able to account for the spontaneous emission of light quanta by an atom, and for the dispersion or scattering of light by an atom. A generalisation of the theory, given by Waller‡, accounts for the Compton effect.

* Cf. Sommerfeld, *Wave Mechanics*, p. 77.
† *Proc. Roy. Soc.* vol. CXIV, p. 243.
‡ *Z. Physik*, vol. LVIII, p. 75.

CHAPTER VI

THE HELIUM ATOM AND THE HYDROGEN MOLECULE

SECTION I

THE IONISED HYDROGEN MOLECULE

There is a well-known and beautiful little experiment that shows the interchange of energy between two vibrating systems. Two pendulums are hung up together, side by side, on a string that is stretched horizontally between two fixed supports. If one pendulum is set in motion, swinging to and fro, then its motion will gradually die down, while, at the same time, the second pendulum begins to move, and swings with ever-increasing amplitude, until the first pendulum comes to rest. Then the process will be reversed, the motion of the second pendulum dying away, and that of the first increasing. The process will be continued till both pendulums are brought to rest by the resistance of the air and by the other frictional forces.

The dynamical system, that the two pendulums taken together comprise, is clearly not vibrating in any normal mode. A system is vibrating in a normal mode, if *every point* of the system is in the same position "now," as it will be in time τ from now, and in time 2τ, and so on. τ is called the "period" of the normal mode, and $1/\tau$ the frequency. This particular system is capable of vibrating in only two normal modes. If the two pendulums have the same length and the same mass, and if they are both hung at the same distance from the middle of the string, so that everything is symmetrical between them, then these two normal modes are particularly simple. In one, the two pendulums swing with the same amplitude, and in phase; when one swings to the right, so does the other, and *vice versa*. That this is a possible motion, and that it will go on indefinitely, is clear from considerations of symmetry; for any cause that might operate

to make pendulum A give up its energy to pendulum B would operate just as much the other way round. In the other possible normal mode, the two pendulums are swinging with equal amplitude, and opposite phase, when one swings to the right the other swings to the left.

The frequencies of the system in these two normal modes are not equal to one another, and neither is equal to the frequency with which either pendulum would oscillate, were the other one absent. Let us call this latter frequency ν, and the frequency with which the pendulums vibrate in phase ν_1, and with opposite phase ν_2. One can see that ν_2 is greater than ν and ν_1 less than ν. For when they are swinging in opposite phase, the pendulums are, so to speak, pulling one another back all the time, and so increasing the restoring couple. The frequency must therefore be greater than it would be in the absence of one of the pendulums. When the pendulums are swinging in the same phase, the opposite is the case; the pendulums help each other to swing outwards, the restoring couple is decreased, and so the frequency is less than it would otherwise be. One can also see that the amount by which ν_1 and ν_2 differ from ν depends on the strength of the coupling between the pendulums. For instance, if the string on which the pendulums are hung be fairly tight, and the two pendulums are hung very near to opposite ends of the string, then ν_1 and ν_2 will not differ from ν by as much as they would if the pendulums were hung nearer to the middle of the string.

It is on the existence of these two different frequencies ν_1 and ν_2 that the slow exchange of energy from one pendulum to the other and back depends. If any system is capable of vibrating in a certain number of normal modes, then the most general vibration possible to it is obtained by superimposing these normal modes, one upon the other. In our case, if θ_1, θ_2 are the angles through which the two pendulums have swung at any moment, then the equations, giving θ_1 and θ_2, for the first normal mode (when the two vibrate in phase) are

$$\theta_1 = A \cos 2\pi (\nu_1 t + \alpha), \qquad \theta_2 = A \cos 2\pi (\nu_1 t + \alpha).$$

In the second normal mode (in which the pendulums swing in opposite phase),

$$\theta_1 = B \cos 2\pi (\nu_2 t + \beta), \qquad \theta_2 = -B \cos 2\pi (\nu_2 t + \beta).$$

A and B are arbitrary amplitudes, α, β are arbitrary phases. The most general possible vibration, obtained by adding together these two, is

$$\left.\begin{aligned} \theta_1 &= A \cos 2\pi (\nu_1 t + \alpha) + B \cos 2\pi (\nu_2 t + \beta) \\ \theta_2 &= A \cos 2\pi (\nu_1 t + \alpha) - B \cos 2\pi (\nu_2 t + \beta) \end{aligned}\right\} \ldots\ldots(1).$$

The angular velocities of both pendulums can be found by differentiating these equations with respect to t. Now suppose we start the system swinging at time $t = 0$, with one pendulum at rest in its position of equilibrium, and the other pulled aside through an angle ϵ. Then at time $t = 0$, say, we must have

$$\theta_1 = \dot{\theta}_1 = 0, \qquad \theta_2 = \epsilon, \qquad \dot{\theta}_2 = 0.$$

The constants A, B, α, β are therefore determined. We find that

$$\alpha = \beta = 0; \qquad A = -B = \tfrac{1}{2}\epsilon.$$

Writing (1) in a slightly different form, then, we have for θ_1, at any time t,

$$\theta_1 = -\epsilon \sin 2\pi \frac{\nu_1 + \nu_2}{2} t \sin 2\pi \frac{\nu_1 - \nu_2}{2} t \quad \ldots\ldots(2.1),$$

and for θ_2, $$\theta_2 = \epsilon \cos 2\pi \frac{\nu_1 + \nu_2}{2} t \cos 2\pi \frac{\nu_1 - \nu_2}{2} t \quad \ldots\ldots(2.2).$$

Now, ν_1 and ν_2 are only slightly different from ν and from each other. Therefore the second factor in (2.1) and (2.2) has a very much longer period than the first. Each of the expressions (2.1) and (2.2) then represents a vibration with frequency very nearly equal to ν, and with varying amplitude

$$\epsilon \begin{matrix} \sin \\ \cos \end{matrix} 2\pi \frac{\nu_1 - \nu_2}{2} t.$$

While the amplitude of the one increases, the amplitude of the other decreases. In fact, a measurement of the time that it takes for the energy to go over from one pendulum to the other

and to come back again amounts to a measurement of $\nu_1 - \nu_2$. If the coupling between the two pendulums is strong, this time will be shorter than if it were weak.

This interchange of energy is characteristic of any pair of vibrating bodies that have the same frequency and are coupled together in some way that allows energy to pass slowly from one to the other. Another example is afforded by two identical wires, both stretched on a fairly rigid frame that is nevertheless capable of vibrating a little, and so of communicating energy from one to the other. The frame is supposed to be symmetrical about the plane drawn equidistant from the two wires, and the wires to be parallel to each other. The system is rather more complicated than that consisting of the two pendulums, because each wire separately is capable of vibrating with an infinite number of different frequencies. But if we start one wire vibrating with one of its characteristic frequencies, then it will slowly set the other wire vibrating with the *same* frequency, while its own vibrations die down; then, its vibrations will increase in amplitude again, while those of the second wire die down. Further, corresponding to any possible frequency ν with which a single wire can vibrate, there are two possible normal modes of the system comprised by the two wires, in one of which the wires vibrate in the same phase, and in the other of which they vibrate in opposite phase. The two normal modes have different frequencies, one being less than ν, and the other greater than ν, as before.

Now let us consider an ionised hydrogen molecule. The reader will remember that all that can be known about the electron in a hydrogen atom is summed up by the behaviour of a wave. This wave suffers internal reflection at the "boundary" of the atom, i.e. at a distance from the nucleus of ϵ^2/E, where E is the ionisation energy of the atom. The wave is therefore only able to vibrate with one of a certain definite series of frequencies ν_n, and since a wave function, vibrating with frequency ν, always describes an electron with energy $h\nu$, we deduce that the electron is only capable of existing in the atom if its energy has one of the values

$h\nu_n$. If the electron has the lowest of these energies, we say that the atom is in its normal state. Further, if ψ be the amplitude of the wave, $|\psi|^2\,dxdydz$ is equal to the probability that the electron is in the volume element $dxdydz$, and therefore, if the wave function is intended to describe a state of affairs in which it is *certain* that there is an electron in the atom, i.e. that the atom is not ionised, then we must have

$$\int |\psi|^2\,dxdydz = 1.$$

A wave for which

$$\int |\psi|^2\,dxdydz = a^2$$

we shall call a wave of amplitude a.

Now an ionised hydrogen molecule consists of a single electron in the field of two nuclei. We shall suppose for the moment that the two nuclei are fixed, rigidly, at a distance R from each other. Further, that R is greater than the "radius" of the atom. Then the potential V of the field that the electron moves in is shown in Fig. 10. The curved line in the upper part of the figure shows V plotted against the distance along a line through the two nuclei. The horizontal dotted line $X_1X_2X_3X_4$ represents the energy of the electron, and the shaded regions between X_1X_2 and X_3X_4 the regions of positive kinetic energy in which, according to the classical theory, the electron must be.

The wave mechanics, however, gives quite a different picture. The de Broglie wave can vibrate in either of the two shaded regions with any of the frequencies ν_n. However, at the boundary of each atom, where the wave is reflected, the amplitude of the wave does not suddenly become zero, but begins to die away exponentially. There is therefore some coupling between the waves vibrating in the two atoms; it is possible for the one wave to hand over its "motion" to the other. The waves in the two atoms therefore will behave like the waves in the two wires that we have discussed. If, initially, one wave is vibrating, and the other is at rest, then the wave in the first atom will slowly die down, and a wave will spring up in the other atom and

vibrate with increasing amplitude. This can only mean that if we *know* that the electron is initially in the first atom, then after a time t there will be a probability that it has got into the second atom, and this probability will slowly increase, and then die away again. If A, B, be the amplitudes of the two waves at any

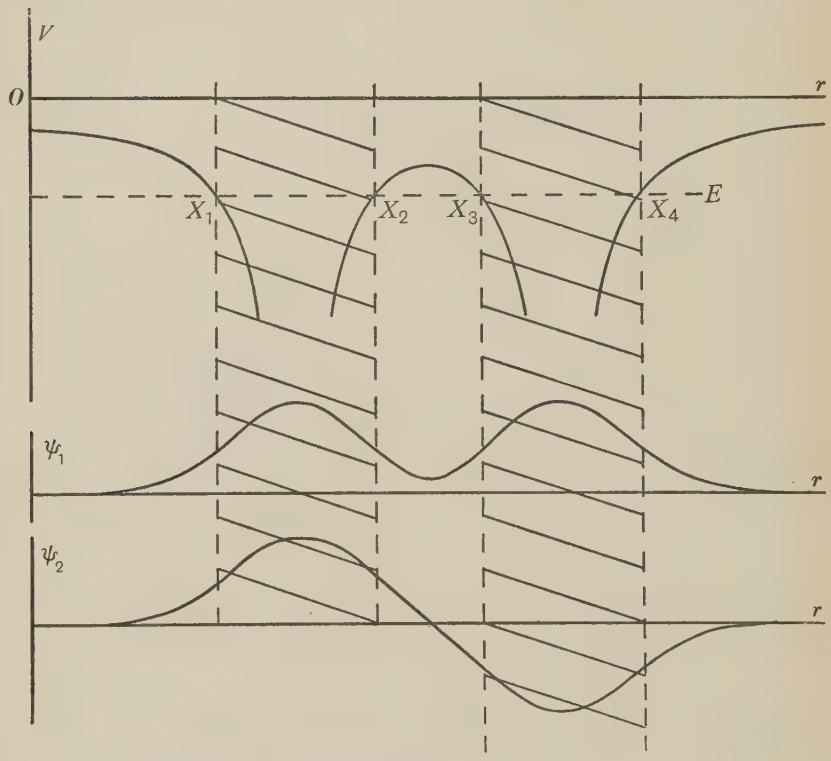


Fig. 10.

moment, then A^2 is the probability that the electron is in the first atom, and B^2 the probability that it is in the second. If $A^2 + B^2$ did not remain constant, the theory would make nonsense, for the probability (equal to unity) that we have an electron in one or the other atom must remain constant. However, we can see by analogy that this will be so, because

$A^2 + B^2$ behaves like the *energy* of a pair of material waves. It may further be proved from the wave equation*.

This fact that the electron appears to change over from one atom to the other is of no great physical importance. If the atoms are, say, a centimetre apart, the time required is of the order of millions of years; and if the atoms are close together, as in a molecule, there is no way of observing the exchange. What is important is this: the state of affairs in which the wave starts vibrating in one atom only, and then hands over its motion to the wave in the other atom, is not a normal vibration of the system consisting of the two waves. Corresponding to every characteristic frequency ν in which the wave function for a single hydrogen atom can vibrate, there will be a pair of normal modes for the molecule; in one, the waves in the two atoms will vibrate up and down in the same phase, and with the same amplitude; in the other they will vibrate in opposite phase. The two normal modes will have different frequencies ν_1, ν_2, and ν_2 will be greater than ν, and ν_1 less than ν. Both normal modes are shown in Fig. 10, in which ψ is shown plotted against the distance, along a line through the two nuclei. ψ falls off exponentially outside the shaded regions.

We deduce that, corresponding to any stationary state of energy E, of an isolated atom, there are two stationary states for an electron in the field of two nuclei, and one has energy $E_1 = h\nu_1$ greater than E, the other energy E_2 less than E. The wave function, that represents at time t a wave vibrating in the first atom and not in the second, represents a state of affairs in which both normal modes are excited, and therefore the electron may have energy either E_1 or E_2. It follows that if we know that the electron is in one or other of the atoms at any instant of time, then we cannot know which of its two possible energy values it has. This after all is not surprising; when the atoms are far apart, the energy levels are so close together as to be indistinguishable; when on the other hand the nuclei are near to each other, the question as to which atom the electron is in

* Cf. Appendix, Note 4.

becomes rather meaningless, and it seems plausible in any case, that if an experiment were made to find out where the electron was, the electron would itself be so disturbed that it might well be knocked from one stationary state to another. This impossibility of knowing all about the electron at any moment is another example of the Uncertainty principle.

An electron, then, free to move in the field of two nuclei, can exist in certain stationary states, of which the energy levels lie close to those of the hydrogen atom. The arguments that we have used to arrive at this result are of course nothing more than analogies, which show what type of solution a certain differential equation should have. There is no new principle involved. The problem is simply that of the behaviour of an electron in an electrostatic field of force. Mathematically, the problem is to find for what values of E the differential equation

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{\epsilon^2}{|\mathbf{r}-\mathbf{a}|} + \frac{\epsilon^2}{|\mathbf{r}-\mathbf{b}|}\right)\psi = 0$$

has a solution that falls off exponentially for increasing r. $\mathbf{a}$ and $\mathbf{b}$ are the positions of the two nuclei. A mathematical discussion has been given by A. H. Wilson* and to this the reader is referred.

Now, up till the present we have considered the nuclei to be fixed. This is of course not the case; they are free to move, and an actual stable molecule will only be formed if the energy of the whole system is a minimum.

Two terms contribute to the energy of the system: there is firstly the potential energy of the nuclei, due to their mutual repulsion. If the nuclei are distant R apart, this will amount to ϵ^2/R. In Fig. 11 the energy of the system is plotted against R. The term ϵ^2/R is shown by the dotted line II.

Secondly there is the energy due to the electron. The amount of this will depend firstly upon R, and secondly upon the stationary state that the electron is in. The energies E_1, E_2 in the two lowest of the stationary states are shown plotted against the

* Wilson, *Proc. Roy. Soc.* A, vol. CXVIII, p. 635.

distance R in Fig. 11. For large R, when there is a very little interaction, both will tend to E, the energy of the normal state of the hydrogen atom. With decreasing R the energy E_2 of the stationary state in which the waves in the two atoms vibrate in phase decreases; the energy E_1 of the other stationary state increases.

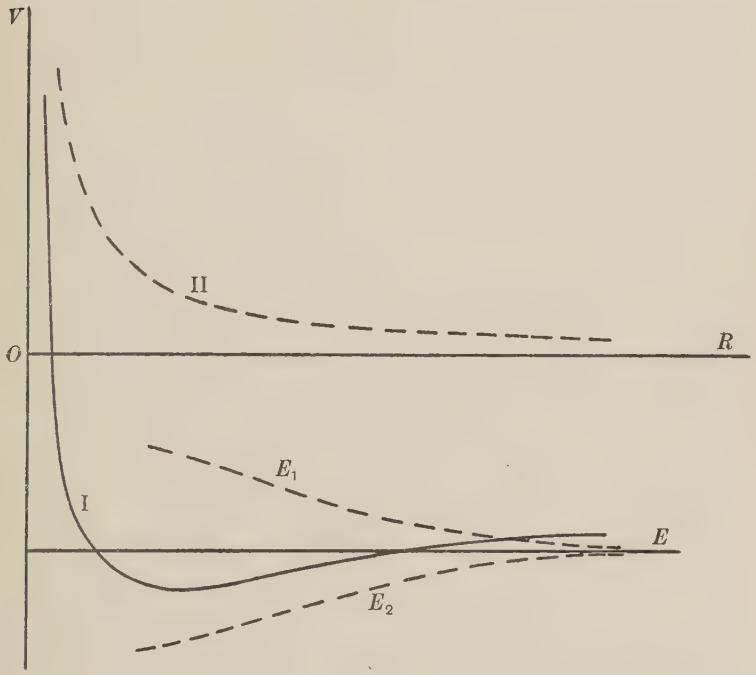


Fig. 11.

The energy of the whole molecule is the sum of the energy of the electron, and the mutual energy of the two nuclei. If the electron is in the stationary state (1), then this total energy is shown plotted against R by the full line marked I in Fig. 11. The energy is seen to pass through a minimum for a certain value R_0 of R. Therefore if the nuclei are a distance R_0 apart, and the electron is in a state of lowest possible energy, then any possible

displacement will increase the energy of the system, and a stable molecule is formed.

If the electron has energy E_1, no minimum occurs and no stable molecule can be formed.

We must now consider how a molecular ion can be formed from a hydrogen nucleus and a hydrogen atom in its normal state. Suppose the atom and nucleus are approaching each other in a gas. The velocity of the nuclei will be slow compared to the motion of the electrons, and at any moment we may consider them at rest. When the two nuclei are close together, the wave in the atom will begin to die down, and a wave will spring up round the other nucleus. This, we have seen, means that the electron may have either the energy E_1 or E_2. Now, unless the two nuclei can get rid of their excess kinetic energy, no molecule can be formed. But if when they are distant R_0 apart, radiation or some third body carries off their excess energy, then the pair will be left with energy either $E_2 + \epsilon^2/R_0$ or $E_1 + \epsilon^2/R_0$. In the former case a molecular ion will be formed; in the latter, the atom and the nucleus will repel each other and become free again.

It is difficult to see what happens to the normal mode of frequency ν_1 when the molecule is formed. Before the excess energy of the nuclei was removed, both normal modes were excited; in the stable molecule, only one. A complete explanation cannot be given without using the results of the remainder of this chapter, and of Chapter VII. The discussion will however be given here.

We describe the positions of the nuclei by wave packets; if $\mathbf{R}$ be the distance apart of the nuclei, let $w_M(\mathbf{R})$ be a wave function describing the state of the nuclei when bound in the molecule, and $w_I(\mathbf{R})$ a wave function when they are moving towards each other, and $w_S(\mathbf{R})$ the wave function when they are moving apart. Then before the collision the wave function of the whole system is

$$w_I(\mathbf{R})\,\psi_a(\mathbf{r}),$$

and after the collision, the wave function is

$$w_S(\mathbf{R})\,[A\psi_a(\mathbf{r}) + B\psi_b(\mathbf{r})] + Cw_M(\mathbf{R})\,\psi_M(\mathbf{r}),$$

where $\psi_a(\mathbf{r})$ is the wave function of the electron on the nucleus a, $\psi_b(\mathbf{r})$ the wave function on the nucleus b, and $\psi_M(\mathbf{r})$ the wave function of the electron in the stable molecule, vibrating in the normal mode with frequency ν_1. $|C|^2$ is the probability that a molecule is formed, $|B|^2$ the probability that the electron changes its nucleus.

SECTION II

THE INTERACTION BETWEEN TWO PARTICLES

The wave mechanics that we have developed in the preceding pages is capable of predicting the behaviour of an electron or of a beam of electrons in a field of force but it is not capable of taking into account the interaction *between* two electrons. To describe therefore the helium atom, the hydrogen molecule, or such a phenomenon as the collision between two electrons, some new generalisation must be introduced. In order to make clear what this generalisation is, we shall consider two electrons moving, not in ordinary three-dimensional space, but in one-dimensional space. In other words, the two electrons are free to move along a straight line, like two beads which can slide up and down a wire. It may be supposed that the beads can pass over each other freely. Most of the essential properties of a pair of electrons in real space can be derived from this simplified model.

We shall suppose that the particles are identical, both having mass m and charge ϵ. We shall denote one particle by A, and the other by B. Let us take a fixed point S on the line, from which we can measure distance, so that if SA and SB are given, the positions of the particles are known. Let us suppose, further, that there is an electrostatic field present, so that the potential energy of a particle, distant x from S, is $u(x)$. If one particle is distant x from S, and the other particle distant y, the potential energy of the pair of them is

$$u(x) + u(y).$$

Let there be also some interaction between the particles, so that when they are distant r from each other they have potential energy $U(r)$. Then, if A is distant x from S, and B is distant y, their mutual potential energy is $U(|x-y|)$. The potential energy $V(xy)$ of the pair, due to all causes, is

$$V(xy) = u(x) + u(y) + U(|x-y|).$$

It is important, and will be required later, that the potential energy of the pair is the same, whether it is A that is distant x from S, and B distant y, or whether it is B that is distant x from S, and A distant y. In other words,

$$V(xy) = V(yx).$$

Now, the force acting on the particle A, if it be distant x from S, is

$$-\frac{\partial}{\partial x} V(xy).$$

Therefore the equation of motion of the particle, giving the way in which x changes, is, according to the Newtonian mechanics,

$$m\ddot{x} = -\frac{\partial V}{\partial x}.$$

Similarly, if y be the distance of the other particle from S, then

$$m\ddot{y} = -\frac{\partial V}{\partial y}.$$

Now these two equations are exactly the equations of motion of a *single* particle moving in a plane, under the influence of a field of force of potential $V(xy)$, x and y being the Cartesian coordinates of the particle. The two problems, therefore, that of finding the motion of a pair of particles, each with one degree of freedom, and that of finding the motion of a single particle with two, are mathematically the same. If

$$x = f(t), \qquad y = g(t)$$

represents a possible motion for the particle moving in a plane, it also represents a possible motion for the pair of particles on a line.

Now let us return to the wave mechanics. We have not yet decided how to treat a pair of particles that interact with each other, but we do know how to treat the motion of a particle in a plane. We describe our knowledge of the particle by a wave function $\psi(xy)$. The wave function satisfies the differential equation

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\psi - V(xy)\,\psi \quad \ldots\ldots(3),$$

and also certain boundary conditions. We derive our knowledge of the particle from the assumption that $|\psi(xy)|^2\,dx\,dy$ is equal to the probability that the particle lies in the surface element $dx\,dy$. In other words, $|\psi(xy)|^2\,dx\,dy$ is equal to the probability that the x coordinate of the particle has a value lying between the two lengths x, $x+dx$, and that the y coordinate has a value between y and $y+dy$.

Now, on the classical theory, the equations determining the motion of a pair of particles, each with one degree of freedom, are the same as those which determine the motion of a single particle with two degrees of freedom. Let us assume that this is also true in the wave mechanics. Our knowledge of a pair of particles will then be described by a wave function $\psi(xy)$, satisfying (3), and $|\psi(xy)|^2\,dx\,dy$ will give the probability that the distance SA lies between the values x, $x+dx$, and that, at the same moment, SB lies between y and $y+dy$. These assumptions are, of course, only justified if they yield results in agreement with experiment, which, as a matter of fact, they do.

The first application that we shall make of these new ideas will be to determine the possible energy levels that our pair of particles can have, if they move on a line of limited length, and are reflected at the two ends. We shall suppose the line bounded at the two points $x=0$, $x=a$. Then the problem is clearly the same as that of determining the energy levels of a single particle moving in a plane, and confined within the square formed by the lines $x=0$, $x=a$, $y=0$, $y=a$. The solution of this problem we have considered already. The wave function that tells us all that we can know about the particle must vanish on the

boundary of the square. Therefore it can only vibrate with certain characteristic frequencies. Therefore the particle can only have certain energy values. We conclude that the total energy of a pair of particles can only have certain discrete values. Our mode of description does not tell us how much of the energy each particle has, only the energy of the two of them together.

The wave equation, satisfied by the wave function for a particle with energy E, moving on a square, is

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0 \qquad \text{.....(4),}$$

and ψ must vanish at the boundary of the square. There is considerable similarity between this equation and the equation satisfied by a membrane stretched tight in a square frame. Let us suppose that T is the tension of the membrane, and ρ the mass per unit area, which may be uniform, or may vary from point to point. Then if the membrane is vibrating in a normal mode of frequency ν, the equation satisfied by Z, the displacement, is

$$\frac{\partial^2 Z}{\partial x^2}+\frac{\partial^2 Z}{\partial y^2}+\frac{4\pi^2\nu^2\rho}{T}Z=0.$$

If V is zero, then if we take ρ constant, this equation is of exactly the same form as (4). If V is not zero, then the two equations are not quite the same, because the refractive index depends on E for de Broglie waves, but is independent of ν for waves in a stretched membrane. However, the analogy is helpful in enabling us to picture the various ways in which ψ can vibrate.

Let us suppose first of all that there is no force on the particles, and no interaction between them. Then V in equation (4) is zero. The vibrations of the wave function ψ will be similar to those of a stretched membrane of uniform density.

Now if such a membrane is vibrating in a normal mode, it has a certain number $l-1$ of nodal lines spaced at equal distances between $x=0$, $x=a$, and a certain number $n-1$ spaced at

equal distances between $y = 0$, $y = a$. This normal mode we shall call (l, n) normal mode. The displacement of the membrane in the (l, n) normal mode is

$$Z = Z_0 \cos 2\pi\nu t \sin \pi lx/a \sin \pi ny/a.$$

The (6, 3) normal mode is illustrated in the figure.

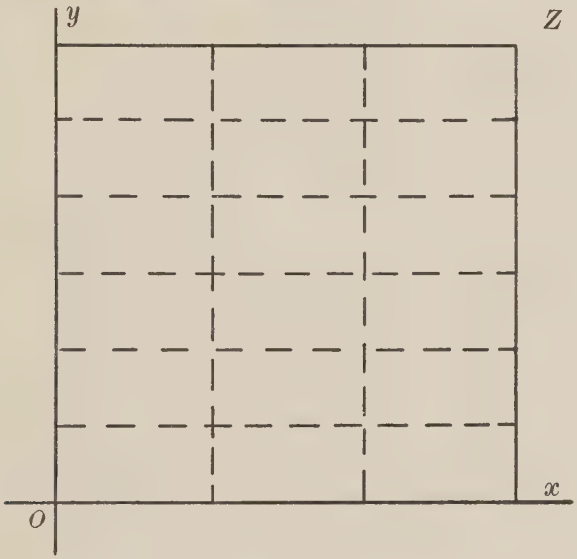


Fig. 12.

The corresponding normal vibration of ψ is

$$\psi = \frac{2}{a} e^{2\pi i\nu t} \sin \pi lx/a \sin \pi ny/a \qquad \ldots\ldots(5)$$

with $$\nu = h\,(l^2 + n^2)/8ma^2.$$

The amplitude $2/a$ is inserted in order that $|\ \psi\ |^2$ integrated over all x, y shall be unity. Applied to the particle moving in a square, the wave function describes a state of affairs in which the energy is $h^2\,(l^2 + n^2)/8ma^2$. Applied to the pair of particles moving on a line, the wave function describes a state of affairs in which the sum of their energies has this value.

The wave function (5) is the product of the wave function of particle A, with energy $h^2l^2/8ma^2$, and of the wave function of the particle B, with energy $h^2n^2/8ma^2$. If there is no interaction between the two particles, therefore, the energy of the pair is equal to the sum of their individual energies, and the wave function of the pair is equal to the product of their individual wave functions. As we shall see, when there is interaction between the particles, the wave function for the pair can no longer be expressed as a product.

The wave function (5) is degenerate. It is clear that the (ln) vibration has the same frequency as the (nl) vibration in which there are $n - 1$ nodes between $x = 0$, $x = a$, and $l - 1$ between $y = 0$ and $y = a$. Therefore, to one characteristic frequency, there are two separate normal vibrations. The normal modes for which l and n are equal, however, are not degenerate.

Suppose now that the particles move in a field, such that potential energy of a particle distant x from S is $u(x)$. Then the potential energy $V(xy)$ of the pair of particles is

$$V(xy) = u(x) + u(y) \qquad \text{.....(6).}$$

It is clear that the wave function for the pair of particles will still be the product of the wave functions of the particles individually. For let $\psi(x)$ be the wave function of one of the particles; then ψ will satisfy the wave equation

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}[\epsilon - u(x)]\psi = 0,$$

where ϵ is the energy of the particle. ϵ will have a series of characteristic values $\epsilon_1, \epsilon_2, \ldots$, and the corresponding wave functions $\psi_1, \psi_2, \ldots$ will have 0, 1, 2, ... nodes between $x = 0$ and $x = a$. These nodes will not, however, be at equal intervals.

$\psi(y)$, the wave function for the other particle, will satisfy the equation

$$\frac{d^2\psi}{dy^2} + \frac{8\pi^2 m}{h^2}[\epsilon' - u(y)]\psi = 0.$$

Its energy ϵ' will have the same series of characteristic values.

Now, if E in equation (4) is equal to one of the values $\epsilon_l + \epsilon_n$, then

$$\psi(xy) = \psi_l(x)\,\psi_n(y)$$

is a solution of (4). Thus, as before, the wave function for the pair of particles is the product of their separate wave functions. The wave function has $l-1$ nodal lines between $x=0$ and $x=a$, and $n-1$ between $y=0$ and $y=a$.

The same degeneracy exists as before, the (ln) normal mode having the same frequency as the (nl).

Suppose now that there is a small interaction between the particles. For simplicity we may suppose the external field absent, and that V vanishes except when $|x-y|$ is small (i.e. when the particles are near together). The vibrations of the wave function that describe the pair of particles will be similar to the vibrations of a stretched membrane, of uniform density except in the neighbourhood of the diagonal line, $y=x$, in which neighbourhood ρ is slightly decreased. We shall first state without proof how such a membrane will behave. The wave function ψ behaves similarly. A proof that if ψ obeys the wave equation, its behaviour is as we shall state, is given in the Appendix (Note 5).

Let us suppose that we start the membrane vibrating in the (ln) mode of vibration, with $l-1$ nodes between Oy, xZ, and $n-1$ between Ox, yZ. Then, owing to the ridge of increased density along OZ, it will not continue vibrating in this way; but the (ln) vibration will gradually die down, and the (nl) vibration be excited in its stead. Then the energy will return to the (ln) vibration, and so on. The process is similar to the interchange of energy between the two pendulums that we considered in Section 1. There, energy was transferred from one vibrating system to another. Here, energy is transferred from one mode of vibration of the same system to another.

In the normal modes of the system consisting of two pendulums, the two pendulums swing together with the same amplitude, in phase, or in opposite phase. The two normal modes

have different frequencies. In the same way, neither the (ln) nor the (nl) vibrations are true normal modes of the unhomogeneous membrane. Corresponding to two numbers l, n there are a pair of normal modes, in one of which the (ln) and the (nl) vibrations are superimposed with the same phase, in the other with opposite phase. The frequency ν_1 for the former will be slightly less than the (ln) frequency for the homogeneous membrane, the frequency ν_2 of the latter will be slightly greater. The displacements in the two normal modes are

$$Z = Z_0 \cos 2\pi\nu_1 t \,[\sin \pi lx/a \sin \pi ny/a + \sin \pi ly/a \sin \pi nx/a],$$

$$Z = Z_0 \cos 2\pi\nu_2 t \,[\sin \pi lx/a \sin \pi ny/a - \sin \pi ly/a \sin \pi nx/a].$$

It will be noticed that this splitting of one frequency into two only occurs if n is not equal to l. If n and l are equal, the frequency is slightly changed, but there is no splitting.

The wave function ψ, as shown in the Appendix (Note 5), has normal modes similar to those of the membrane. Neither the (ln) nor the (nl) vibrations are true normal modes; there are two possible normal vibrations, with slightly differing frequencies ν_1, ν_2. The wave functions in these vibrations are

$$\psi_1 = e^{2\pi i\nu_1 t} \,[\sin \pi lx/a \sin \pi ny/a + \sin \pi ly/a \sin \pi nx/a] \quad \ldots(7.1),$$

$$\psi_2 = e^{2\pi i\nu_2 t} \,[\sin \pi lx/a \sin \pi ny/a - \sin \pi ly/a \sin \pi nx/a] \quad \ldots(7.2).$$

We deduce that, if ϵ_1, ϵ_2, ... are the characteristic energies of a single particle, then corresponding to any energy $E = \epsilon_l + \epsilon_n$ possible to the pair without interaction, there are two energies E_1 and E_2 possible with interaction. This splitting into two energies does not occur if $l = n$.

There is no difficulty in generalising these results to apply to a pair of electrons, each with three degrees of freedom. We use, instead of a wave function $\psi(xy)$, a wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$. $\mathbf{r}_1$, $\mathbf{r}_2$, denote the positions of the two electrons. $|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$, is the probability that one electron is in the volume element $d\mathbf{r}_1$ and the other in the volume element $d\mathbf{r}_2$. Instead of the wave equation (3), ψ will satisfy

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2)\psi - V(\mathbf{r}_1\mathbf{r}_2)\psi \quad \ldots\ldots(8).$$

If there is no interaction between the particles, and if ϵ_n, ψ_n, and ϵ_l, ψ_l are their energies and wave functions separately, then the wave function of the pair is

$$\psi_n(\mathbf{r}_1)\,\psi_l(\mathbf{r}_2),$$

and the energy $\epsilon_n + \epsilon_l$. If there is a small interaction, then the wave function can vibrate in two normal modes, with slightly different frequencies. The wave functions in these two normal modes are (omitting the frequency factor)

$$\psi = \psi_n(\mathbf{r}_1)\,\psi_l(\mathbf{r}_2) + \psi_n(\mathbf{r}_2)\,\psi_l(\mathbf{r}_1) \qquad \text{.....(9),}$$

and

$$\psi = \psi_n(\mathbf{r}_1)\,\psi_l(\mathbf{r}_2) - \psi_n(\mathbf{r}_2)\,\psi_l(\mathbf{r}_1) \qquad \text{.....(10).}$$

The energy of the pair of particles can therefore have either of two values, one slightly above, and the other slightly below the value $\epsilon_n + \epsilon_l$. It need hardly be said that these energy values only occur if the electrons move in a confined space, either in a box or in an atom.

The wave functions represent vibrations in six-dimensional coordinate space. It is possible to write down the wave functions, but impossible to picture the waves. Therefore, in discussing the helium atom and the hydrogen molecule, we shall pretend as before that space is one-dimensional. The results that we shall obtain are true for three-dimensional space.

The helium atom consists of two electrons moving in one another's field and in the field of the nucleus. Let us suppose that each electron has only one degree of freedom. Suppose first that there is no interaction between the electrons. Then each electron moves in a field such as is shown in Fig. 7. The wave function describing the pair of particles will be similar to the wave function describing the motion of a single particle that is constrained to move inside a square *ABCD* by a force that repels it from the edges. The wave function that describes the behaviour of the electrons will fall off exponentially outside the square *ABCD*. It will be capable of vibrating in a certain number of normal modes, and corresponding to each characteristic frequency there will be two independent modes of vibration.

Now let us consider the interaction between the electrons. As we have shown, each frequency of the old system will break up into two, one of which has a wave function of the form (9), and the other of the form (10). The frequencies of many of these normal modes have been calculated*. It is found that stationary states, that possess wave functions of the form (10), have energy levels belonging to orthohelium, and that energy levels having wave functions of the form (9) belong to parhelium. Why it is that spectral lines produced by a transition from an energy level of parhelium to one of orthohelium is never observed will be explained in Section III. We can, however, see at once why it is that the normal state (i.e. the state of lowest energy) must belong to parhelium. If there is no interaction between the two electrons, the state of lowest energy occurs when both electrons are in their lowest state. Now we have seen that energy levels, in which both electrons are in the same state, are not split into two by the presence of the interaction energy. The only possible wave function is of the form (9), since the function of the form (10) vanishes identically. Therefore the state of lowest energy belongs to parhelium.

A hydrogen molecule consists of a pair of electrons, which are free to move in the field of two nuclei. Again, in order to represent the field and the wave functions diagrammatically, we shall suppose that each electron has only one degree of freedom. Suppose first that there were no interaction between the two electrons. Then each electron will move in the field of Fig. 10; both x and y can lie between X_1 and X_2 or between X_3 and X_4. The xy-plane is shown in Fig. 13, with the potentials in which the electrons move to the side. The doubly shaded areas are the only areas in which the electron, according to the classical theory, can go. The squares $ABCD$, $A'B'C'D'$, represent a state of affairs in which both electrons are in the same atom; the squares $PQRS$, $P'Q'R'S'$, a state of affairs when they are in different atoms. The wave function that describes the two electrons will fall off exponentially outside these squares.

* Hersenberg, *Z. Physik*, vol. xxxix, p. 499 (1927).

Now let us take the interaction between the two electrons into account. Classically, this will have the effect of preventing both electrons from being in the same atom, because their

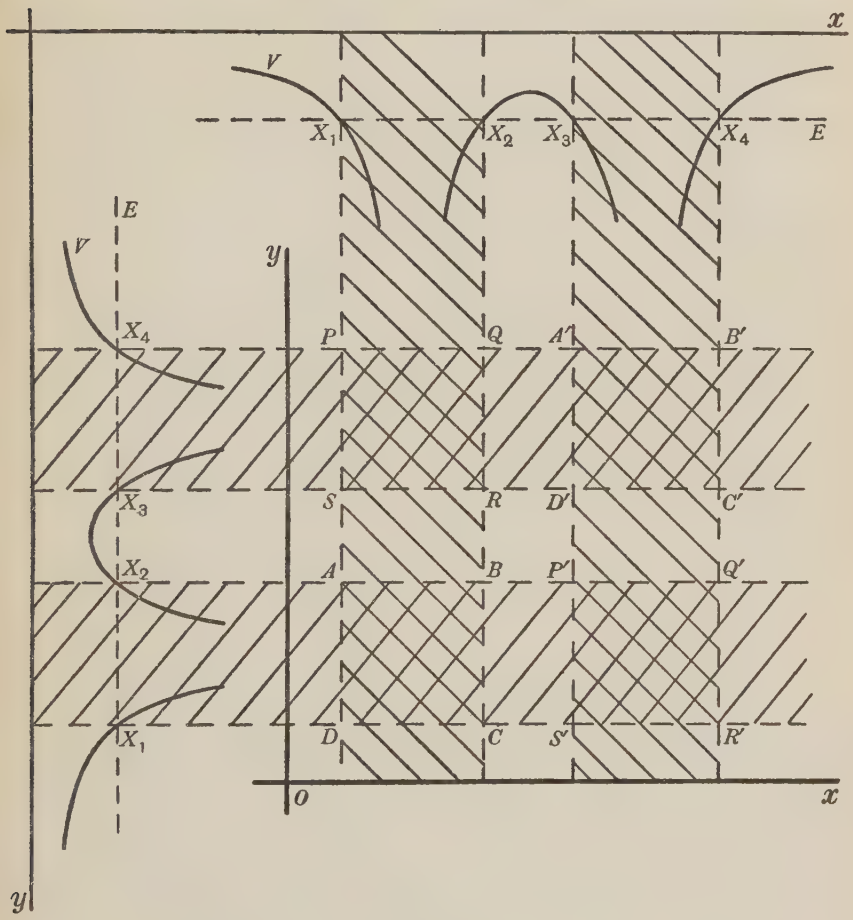


Fig. 13.

mutual potential energy, together with the effect of the nuclei, will be sufficient to make the kinetic energy negative. There will be a small region near the centre of the atom in which they

could both be together. Nevertheless, the effect of the interaction energy will be to make the refractive index imaginary in the greater part of the two squares $ABCD$, $A'B'C'D'$, so that vibrations of the de Broglie wave are no longer possible in these regions; vibrations are only possible in the squares $PQRS$, $P'Q'R'S'$.

If now a vibration is started in the square $PQRS$, then it will not continue indefinitely, because the wave function does not vanish at the boundary of the square, but only starts to fall off exponentially. There will therefore be a very weak oscillation going on in the square $P'Q'R'S'$. We therefore have a state of affairs very similar to the two pendulums with coupling between them. The vibration in the square $PQRS$ will die down, and vibration in the square $P'Q'R'S'$ be excited; then the vibration in the square $P'Q'R'S'$ will die down, and the vibration in the square $PQRS$ be excited again. There are two normal modes of the system, in one of which the vibrations in the two squares are in phase, and in the other of which they have opposite phases. The frequency of the latter will be greater than that of the former, and if the squares were brought closer together, the frequency of the latter would increase and the frequency of the former decrease.

We deduce that, in half the energy levels of a pair of electrons in the field of two nuclei, the energy increases as the distance between the nuclei decreases, and in the other half the energy decreases. The latter half give rise to stable hydrogen molecules in exactly the same way as for the ionised hydrogen molecule considered in Section 1 of this chapter. In the case of the ionised hydrogen molecule, however, the vibrating systems were three-dimensional wave functions vibrating in the neighbourhood of the two nuclei; in this case they are six-dimensional wave functions in two regions of six-dimensional coordinate space, that correspond to the two ways of partitioning the two electrons between the two nuclei*.

* The hydrogen molecule was first discussed on these lines by Heitler and London, *Z. Physik*, vol. XLIV, p. 455 (1928).

SECTION III

EXISTENCE OF NON-COMBINING TERMS

If the interaction between the particles can no longer be considered as small, the formulae (7·1) and (7·2), or more generally (9) and (10), can no longer be considered good approximations to the true wave functions. The nodal lines will be no longer straight, but may become curved. However, in any normal mode in which the wave function can vibrate, there is a certain property that the wave function will satisfy; the vibration will either be symmetrical about the line $x = y$, in which case the displacement at any point (x, y) will be always equal to the displacement at its reflection (y, x) in the line $x = y$, or else the vibration will be antisymmetrical about $x = y$, in which case the displacement at (x, y) will always be equal and opposite to the displacement at the point (y, x). In fact, we can divide the normal modes into two classes, those that are symmetrical about the line $x = y$, and those that are antisymmetrical. In the antisymmetrical ones

$$\psi(xy) = -\psi(yx).$$

In the symmetrical vibrations

$$\psi(xy) = +\psi(yx).$$

It will be seen that (7·2) and (7·1) belong to these two types respectively.

If each electron has three degrees of freedom, then we shall have, in all normal modes, either that

$$\psi(\mathbf{r}_1\mathbf{r}_2) = -\psi(\mathbf{r}_2\mathbf{r}_1),$$

or that

$$\psi(\mathbf{r}_1\mathbf{r}_2) = +\psi(\mathbf{r}_2\mathbf{r}_1).$$

We shall now prove, for electrons with one degree of freedom each, that all the normal modes are described by wave functions either symmetrical or antisymmetrical. We assume that there is no degeneracy, that is to say, that to any one frequency there is only one normal mode. This, as we have seen, is only so if there is interaction between the particles, as in general there is.

ψ satisfies the differential equation (4), which we may write

$$H\,(xy)\,\psi\,(xy) = 0,$$

where $H\,(x, y)$ denotes the operator

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{8\pi^2 m}{h^2}\,(E - V).$$

Now H is not altered if we interchange x and y, therefore it follows that

$$H\,(yx)\,\psi\,(xy) = 0.$$

Let us now write x instead of y, and y instead of x in this equation; we obtain

$$H\,(xy)\,\psi\,(yx) = 0.$$

It follows that $\psi\,(yx)$ is a solution of the differential equation. Now we have assumed that there is no degeneracy, i.e. that to any energy level there is only one wave function. Therefore $\psi\,(xy)$ and $\psi\,(yx)$ cannot be independent solutions, but one must be a multiple of the other. Let, then,

$$\psi\,(xy) = a\psi\,(yx).$$

Now $\int[\psi\,(xy)]^2\,dx\,dy$ is clearly the same thing as $\int[\psi\,(yx)]^2\,dy\,dx$ and we know that neither integral is zero. Therefore,

$$a^2 = 1.$$

Hence

$$a = \pm\,1.$$

The proof is exactly the same when each particle has three degrees of freedom.

It should be noticed that the symmetry of the wave functions depends on the fact that the two particles have the same charge and mass. The symmetry does not occur in the wave function describing particles of different charge or mass.

In Fig. 14 are shown the xy-plane, and possible nodal lines of a wave function constrained to vanish at the edges of a square.

Underneath is shown the displacement ψ of the wave plotted against the distance along a line such as PQP', perpendicular

to the line $x = y$. The curve marked S is the displacement in a typical "symmetrical" normal mode; that marked A, the displacement in a typical antisymmetrical normal mode.

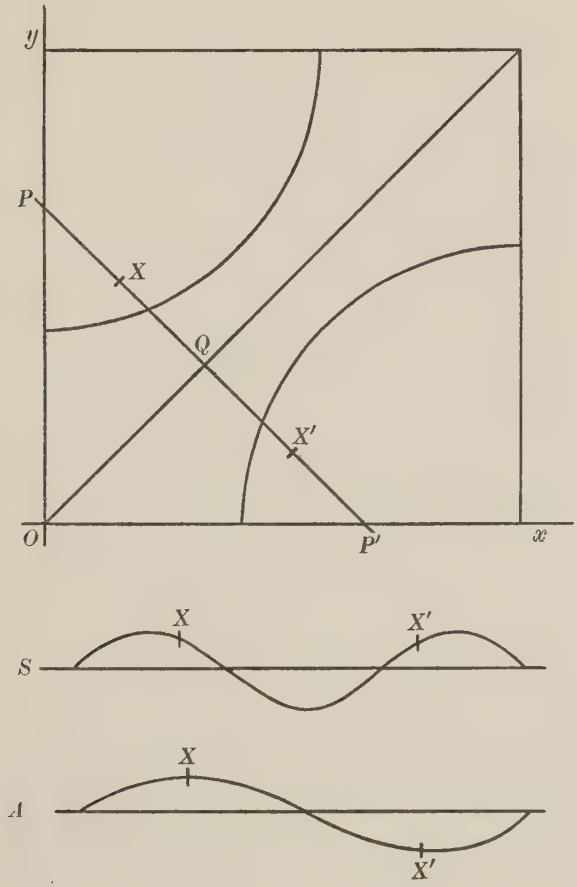


Fig. 14.

If X' is the reflection of any point X in the line $x = y$, then in the S vibration the displacement of X' is equal to that of X, and in the A vibration, it is equal and opposite.

Now the interesting thing about this symmetry is that if we have a pair of electrons in a stationary state, such that they are described by a wave function that is symmetrical in the coordinates of the two electrons, then nothing that we can ever do to them can possibly bring them into a state described by an antisymmetrical wave function, and *vice versa*. This can be seen as follows. If the electrons are initially in a given stationary state, and the wave function is vibrating in the corresponding normal mode, then any disturbance that we may give to the atom will simply excite the other normal modes. The amplitude with which each is excited will give the probability that the atom has gone into the corresponding stationary state. Now any disturbance to which we may subject the atom may be represented by a varying electromagnetic field. Suppose then that we perturb the atom by an electric field of potential $F(x, t)$. Then the potential of the pair of electrons in this varying field will be $\epsilon F(x, t) + \epsilon F(y, t)$. The effect of the field will therefore be to vary the "refractive index" for the waves represented by the wave function $\psi(xy)$. But whatever we do to the atom, the refractive index will always remain the same at the point (x, y) as at the point (y, x). It is impossible to construct a field that will give a different potential energy if the particle A is at x, and the particle B at y, from the potential energy if the particle A is at y and the particle B at x.

Suppose, then, that the wave function is vibrating in a symmetrical normal mode. We perturb the atom, and excite other normal modes. But if we look at Fig. 14, which represents the displacement of the wave function plotted against one of the lines $x + y =$ constant, and remember that whatever we do to the "medium" at T, we must do the same at T', it becomes clear that if a vibration is once symmetrical, it must always remain symmetrical. No antisymmetrical normal modes are excited, and there are therefore no transitions to antisymmetrical states.

We shall now give a formal proof that if a wave function is initially symmetrical it will remain symmetrical, and if it is

initially antisymmetrical it will remain antisymmetrical. The wave function satisfies the differential equation

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2}\right) - V(xy)\,\psi \quad \ldots\ldots(11),$$

where $V(xy)$ is the potential energy of both the interaction between the electrons and the nucleus, and the energy of the electrons in the perturbing field. The operator on the right has the property that if we write x instead of y, and y instead of x, it is unaltered. Now the increase $d\psi$ of ψ in time dt is equal to $\frac{\partial\psi}{\partial t}\,dt$. It follows from (11) that if ψ is initially symmetrical, so that $\psi(xy)$ and $\psi(yx)$ are equal, then the increase in ψ in time dt is also symmetrical. Therefore ψ will remain symmetrical. If, however, ψ is initially antisymmetrical, then $d\psi$ is antisymmetrical and therefore ψ will remain antisymmetrical. It follows that there can be no transitions from symmetrical stationary states to antisymmetrical ones or *vice versa*.

We now see why it is that transitions between states of para- and orthohelium are never observed. Actually, the assumption that

$$V(\mathbf{r}_1\mathbf{r}_2) = V(\mathbf{r}_2\mathbf{r}_1),$$

upon which our proof of the existence of non-combining states is based, is not quite true, because electrons have a small magnetic moment. This "spin" moment will be discussed further in Chapter VIII. Owing to the spin forces, transitions between ortho- and parhelium do probably occur, but not in sufficient intensity to be observed.

The wave functions used so far have described our knowledge of the position of a pair of electrons. In the theory of diatomic molecules, the positions of a pair of nuclei are described by a wave function. If the two nuclei are identical, some of the calculated stationary states of the molecule have wave functions that are symmetrical in the coordinates of the two nuclei, and some are antisymmetrical. In the helium molecule, where the

nuclei are α particles, only the symmetrical energy levels are found in the band spectrum. It is believed that the anti-symmetrical energy levels never occur.

α particles are believed to have no "spin." When the spin of the electron is taken into account (Chapter VIII) it is seen that for electrons also only half the possible energy levels occur.

CHAPTER VII

DYNAMICS OF SYSTEMS CONTAINING MANY ELECTRONS

SECTION I

THE SELF CONSISTENT FIELD

If the experiments of Davisson and Germer, and of G. P. Thomson, had been carried out years ago, before the particle-like nature of cathode rays had been so amply demonstrated in the Wilson Chamber and by other means, it would naturally have been thought that cathode rays were waves in some material medium possessing inertia. But even in the case of light waves, some time before the advent of the wave mechanics, the idea of a material medium was abandoned, because of the difficulty of reconciling it with the Michelson-Morley experiment, which failed to detect any motion of the earth through the medium. It is not surprising therefore that no attempts have been made to find a medium for the de Broglie waves. In this book we have developed the view that there is no medium in any physical sense, and that the waves are merely a convenient device for expressing the results of any possible experiment on the position and velocity of an electron, and have no existence before the experiment is made. This view of the nature of the waves is confirmed by the arguments of the last chapter, for the wave function in "six-dimensional space" that we used to describe the helium atom cannot possibly represent a wave in any medium, but is a quite natural way of representing the probability of a pair of electrons being at two given points.

To many people, however, it is repugnant that waves in six-dimensional space should be used to describe a physical entity such as a helium atom, and it is worth while to enquire just why it is that we cannot confine ourselves to three dimensions, and give each electron its separate wave function. In a helium atom, why should it not be possible to describe one electron by

a wave function $\psi_a(\mathbf{r})$, so that $|\psi_a(\mathbf{r})^2|\,dxdydz$ should be the probability that it is in the volume element $dxdydz$ at the point $\mathbf{r}$? The other electron, similarly, would be described by a wave function $\psi_b(\mathbf{r})$. Why is it necessary to introduce the wave function $\psi(\mathbf{r}_1\mathbf{r}_2)$? Ultimately our answer must be that the method sketched in the last chapter gives results in agreement with experiment, but there are certain reasons which may be cited *a priori*, that show that it cannot be correct to use a separate wave function for each electron.

For the helium atom, however, it is possible to give a description in terms of two wave functions, that is nearly, but not quite, in agreement with experiment. The method is due to Hartree*, and has the very great advantage that for helium and for more complicated atoms the wave functions can be evaluated numerically. An account of this method will now be given, for the simplest case, that of a helium atom.

We assume that each electron has its wave function $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$ vibrating in normal modes with frequency E_a/h, E_b/h respectively. We assume that the wave function ψ_a will satisfy the ordinary Schrödinger wave equation

$$\nabla^2\psi_a + \frac{8\pi^2 m}{h^2}[E - V_a(r)]\psi_a = 0 \qquad \ldots\ldots(1),$$

where $V_a(r)$ is the potential of the field in which the electron a moves. Now we cannot be quite certain what this field is, because it is due to electron b as well as to the nucleus, and we do not know exactly where this electron is. We therefore *assume* that the correct field to use is obtainable by averaging over all possible positions of the electron b, so that $V_a(r)$ is to consist of the field of the nucleus, together with

$$\iiint \frac{1}{|\mathbf{r} - \mathbf{r}'|}|\psi_b(\mathbf{r}')|^2\,dx'dy'dz' \qquad \ldots\ldots(2).$$

Now to begin with we do not know either ψ_a or ψ_b or V_a or V_b, but we can determine them in this way. Let us guess ψ_b, writing down some function of r that we think may be roughly right. Then we can work out $V_a(r)$, and solve the equation (1),

* *Proc. Camb. Phil. Soc.* vol. XXIV, pp. 89, 111, 426 (1928).

finding the characteristic energies E_a and the corresponding wave functions ψ_a. If we wish the electron a to be in the nth stationary state, we must take the nth of these functions. We now know the field that the electron b moves in, obtaining it as before by averaging over all positions of the electron a, giving each position the weight $|\psi_a(\mathbf{r})|^2$. Therefore, we know the wave equation that ψ_b must satisfy, namely, the equation (1), with b written for a. Solving this equation we obtain ψ_b. This ψ_b ought to be the same function as the ψ_b that we started out with. By successive approximations, it is possible to choose ψ_b so that this is the case. ψ_a and ψ_b are then the required wave functions.

This method gives the ionisation potential of helium correct to within 1 per cent. It has also been applied to many of the heavier atoms. The wave functions obtained are used to calculate the scattering of X-rays and of electrons by atoms, and give results in agreement with experiment. The method seems to give a more "picturesque" description of the atom than does a wave function in the six-dimensional coordinate space. We shall now discuss the reasons, apart from the imperfect agreement with experiment, why an exact account of the interaction between two electrons cannot be given on these lines.

SECTION II

We shall return to the pair of particles, moving along a line, that we discussed in the last chapter. Let us suppose that the two particles are moving towards each other, with equal and opposite velocities v. We shall suppose that there is some interaction between them, so that they repel each other when they come close together. Then there are only two things which particles with one degree of freedom can do; they can either pass over each other, and go on, or they can be reflected from one another. According to the classical theory, they will always be reflected unless their kinetic energy is greater than their potential energy at all distances, in which case they will pass over each other; but the wave mechanics, on the other hand,

should give a finite probability of reflection, and a finite probability that they will pass over each other, whatever their initial energies. Let us see whether it is possible to obtain a description of the collision, using a separate wave function for each electron, as we do in describing a helium atom by the method of the last section.

Let $\psi_a(x)$ be the wave function of the first electron, so that $|\psi_a(x)|^2 dx$ is the probability that it lies between the points x and $x + dx$; let $\psi_b(x)$ be the wave function of the other electron. Before the collision, each wave function will have the form of a wave packet, and the wave packets will be moving towards each other, as shown in Fig. 15. The full line gives ψ_a, the dotted line ψ_b. After the collision, each wave packet must have split into two halves, since the wave function must allow a prob-

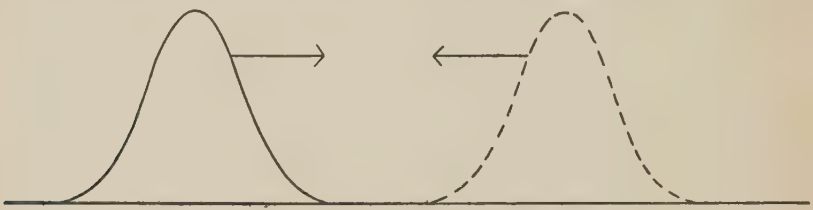


Fig. 15.

ability that the particles have either gone over each other, or have been reflected. The two wave packets are represented in Fig. 16. As before, the full line represents ψ_a, and the dotted line ψ_b. The amplitudes of the reflected wave packets are drawn greater than those of the transmitted wave packets; this would denote a large chance of reflection. The relative magnitude of the reflected and transmitted wave packets would, of course, depend on the strength of the repulsive fields.

Up to a certain point this representation of the collision appears satisfactory; it tells us, at any moment, in what parts of space electron a could be, and how likely it is to be there, and it does the same for electron b. It fails, however, to predict that *momentum* must be conserved on collision; there is nothing in the wave functions which forbids one electron being reflected,

and the other going straight on. The wave function gives a finite probability that electron a should be at the point marked P in Fig. 16, and a finite probability that electron b should be at the same point; it does not express the fact that they may not both be there.

Therefore, by using separate wave functions for the two electrons, it is impossible to express all the observable facts about the collision. We shall now show that if we use one wave function for the two of them, in the way shown in the last chapter, a complete description of the collisions can be obtained.

In the last chapter it was shown that the wave function $\psi(xy)$ describing a pair of particles each with one degree of freedom was the same as the wave function describing a single particle with two. The single particle moves in a plane, and in

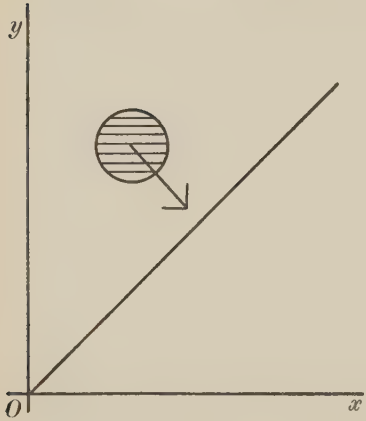
Fig. 16.

the neighbourhood of the line $y = x$ there is a force repelling it from this line. The potential of this force is $V(|x - y|)$, the potential of the interaction between the two particles.

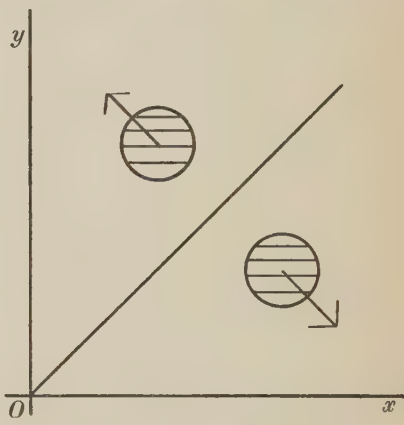
The wave function that describes the two particles moving towards each other will be the same as that which describes the single particle moving parallel to the line $x + y = 0$. Thus before the collision we can represent the pair of particles by a wave packet moving in the xy-plane towards the line $x = y$, as shown in Fig. 17 (a). Now when this wave packet comes to the line $x = y$, it encounters a potential ridge; part therefore will be reflected and part will surmount the ridge and go straight on. After the collision there will be two wave packets, in general of unequal amplitudes, moving away from the line $x = y$, as shown in Fig. 17 (b). It is clear that these two wave packets both represent a state of affairs in which the two packets are moving

away from each other; the reflected wave packet gives the probability that the two particles are reflected from each other, the transmitted one the probability that they pass over each other. The wave function gives no probability that one electron is reflected, and that the other one goes straight on, a state of affairs that would be described by a wave packet moving *along* the line $y = x$. The wave function, therefore, describes *all* that would be observed about the collision.

It is interesting to write down an expression for the wave function before, and after, the collision. Let $w_a(x, t)$ be the



(*a*)



(*b*)

Fig. 17.

wave function, in one-dimensional space, that defines a wave packet moving from left to right with velocity v, and $w_b(x, t)$ the wave functions of a wave packet moving in the opposite direction, with the same velocity. Then before the collision the wave function of the pair of particles is

$$w_a(xt)\, w_b(yt).$$

After the collision, it is

$$Aw_a(xt)\, w_b(yt) + Bw_a(yt)\, w_b(xt).$$

A, B are the transmitted and reflected amplitudes; $|A|^2$ will be the probability that the particles pass over each other, and $|B|^2$ the probability that they are reflected.

SECTION III

THEORY OF THE COLLISION OF ELECTRONS WITH ATOMS

In Chapter I we discussed the collision between an electron and an atom, treating the atom as a static distribution of charge. Even the simplest of these collision problems, that between an electron and a hydrogen atom, is however strictly a two-body problem, and the collision must be described by a wave function in six-dimensional space. We shall treat the collision from this point of view, and show that the former method gives a first approximation to the correct result.

As before, we may represent our knowledge of the electron before the collision by a wave packet, $w_a(\mathbf{r})$, moving towards the atom; and if the atom is in its normal state, our knowledge of the atomic electron will be represented by the wave function $\psi_1(\mathbf{r})$. Let us denote the coordinate of the colliding electron by $\mathbf{R}$, that of the atomic electron by $\mathbf{r}$; then before the collision the wave function for the pair of particles is

$$w_a(\mathbf{R})\,\psi_1(\mathbf{r}).$$

Now after the collision, the atom may either remain in the normal state, or it may be in one of the excited states with energy $E_2, E_3, \ldots$, and wave functions $\psi_2(\mathbf{r})$, $\psi_3(\mathbf{r}), \ldots$. The electron, also, may either be scattered with its original velocity v, or with a decreased velocity, having one of the values, v_n, given by the formula

$$E_n + \tfrac{1}{2}mv_n^2 = E_1 + \tfrac{1}{2}mv^2.$$

If an electron is scattered without loss of energy, we say that it is scattered elastically; otherwise we call the collision inelastic.

In the figure are shown the parts of space in which the electron could be, at some time after the collision. If it were scattered elastically, it would be in the outermost ring; the other rings correspond to inelastic collisions. There are, of course, an infinite number of these rings; only two are drawn.

Now, it is *not* correct to represent the electron after the collision by a single wave function whose amplitude vanishes outside the shaded areas, because our wave function must tell us that *if* the electron is scattered with velocity v_n, then the atom must be left with energy E_n. Let then $w_n(\mathbf{R})$ be the wave function of a circular packet, vanishing except in the nth of the shaded rings, and moving outwards with velocity v_n. Then a wave

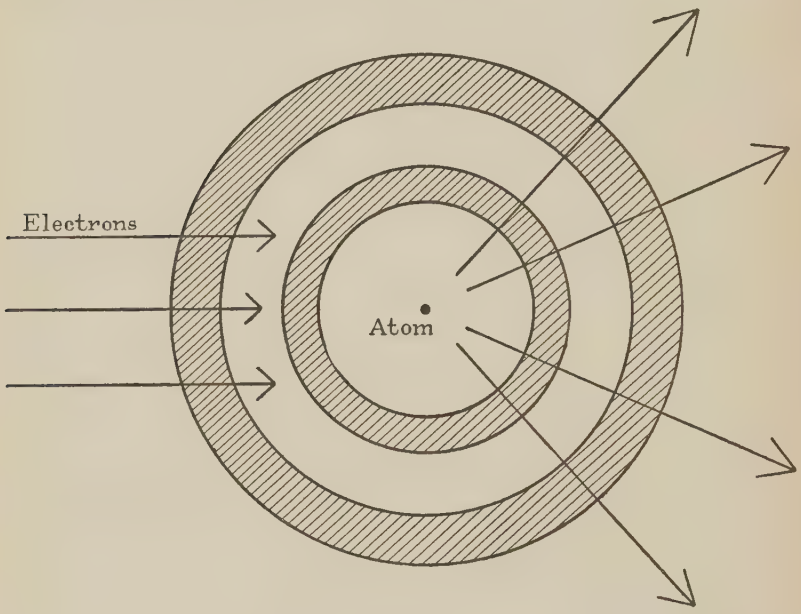


Fig. 18.

function that will describe *all* that can be known about the system after the collision is

$$\psi(\mathbf{Rr}) = \sum_n w_n(\mathbf{R})\,\phi_n(\mathbf{r}) \qquad \ldots\ldots(3).$$

For the square of the amplitude of this wave function will give the probability that the colliding electron is at $\mathbf{R}$, and the atomic electron at $\mathbf{r}$. Now, if we have waited for so long a time after the collision that the rings in Fig. 18, corresponding to different

v_n, do not overlap, then if we take a point $\mathbf{r}$ in the nth ring, all the terms on (3) vanish, except

$$w_n(\mathbf{R})\,\psi_n(\mathbf{r}).$$

This wave function is the product of a wave packet moving outwards with velocity v_n, and of the wave function of the atom in its nth state. The wave function therefore shows that if the electron is scattered with velocity v_n, then the atom is excited to the nth stationary state, energy being therefore conserved.

It will now be shown that a solution of this kind can be obtained from the wave equation, and the actual probabilities of scattering calculated.

In calculating the scattering, it is convenient to represent the incident electron, not by a wave packet, but by an infinite plane wave. Let us write

$$k_1 = 2\pi m v_1/h,$$

so that the incident wave has the wave function*

$$\exp ik_1 Z,$$

where Z is the component of $\mathbf{R}$ along the z-axis. In the same way, let k_n be written for $2\pi m v_n/h$. Let $F_n(\mathbf{R})$ be the wave function of the wave scattered with wave length h/mv_n, corresponding to an inelastic collision. Then $F_n(\mathbf{R})$ must have the asymptotic form, for R much larger than the radius of the atom,

$$F_n(\mathbf{R}) \sim R^{-1} \exp ik_n R . f_n(\mathbf{R}/|\,\mathbf{R}\,|),$$

where f_n represents the amplitude of the wave in any given direction.

The wave function, then, in six-dimensional space, describing the collision, will be

$$\psi(\mathbf{Rr}) = \exp ik_1 Z . \psi_1(\mathbf{r}) + \sum_n F_n(\mathbf{R})\,\psi_n(\mathbf{r}) \ldots\ldots(4).$$

The incident wave represents one electron per unit volume, and therefore v electrons falling on unit area per unit time. In any one of the scattered waves, the probability that an electron is

* A time factor $\exp 2\pi iEt/h$ is omitted.

in the volume element $d\tau$ is $r^{-2} \mid f_n \mid^2 d\tau$, and therefore $v_n r^{-2} \mid f_n \mid^2$ fall on unit area, at distance r from the atom, per unit time. Therefore, our wave function shows that the effective cross-section that an electron must hit, if it is to be scattered into the solid angle $d\omega$ with velocity v_n, is

$$\frac{v_n}{v_1} \mid f_n \mid^2 d\omega.$$

We have now to find a solution of the wave equation of the form (4), and evaluate the amplitudes f_n. The wave equation for a pair of particles in the field of a nucleus has already been given (Chapter VI, equation 8). For a steady wave we may write the equation

$$[H_e + H_a - V_{12}]\,\psi = 0,$$

where

$$H_e = \frac{h^2}{8\pi^2 m}[\nabla_R{}^2 + k_1{}^2],$$

so that $H_e\,\psi = 0$ is the wave equation for an electron in free space, and

$$H_a = \frac{h^2}{8\pi^2 m}\nabla_r{}^2 + E_1 + \epsilon^2/r,$$

so that $H_a\psi = 0$ is the equation for an undisturbed atom, and $V_{12}\,(\mathbf{rR})$ is the interaction energy between the atom and the electron, so that

$$V_{12} = -\epsilon^2/R + \epsilon^2/|\,\mathbf{R} - \mathbf{r}\,|.$$

To solve this equation, we assume that V_{12} is small, and does not appreciably alter the amplitude of the incident wave; the wave function may therefore be expressed

$$\psi\,(\mathbf{rR}) = \exp ik_1 Z\,.\psi_1\,(\mathbf{r}) + \Psi^I\,(\mathbf{Rr}),$$

where Ψ^I, the wave function of the scattered wave, is small. The wave equation then becomes, neglecting small quantities of the second order,

$$[H_e + H_a]\,\Psi^I = V_{12} \exp ik_1 Z\,.\psi_1\,(\mathbf{r}) \qquad \ldots\ldots(5).$$

Now we require Ψ^I expanded in the form

$$\Psi^I = \sum_n F_n\,(\mathbf{R})\,\psi_n\,(\mathbf{r}).$$

Substituting this in (5), we obtain for the unknown functions $F_n(R)$,

$$\sum_n [H_e + E_1 - E_n] \psi_n F_n = V_{12} \exp ik_1 Z . \psi_1(\mathbf{r}),$$

or, writing H_e in full,

$$\sum_n \left[\frac{h^2}{8\pi^2 m} (\nabla_R^2 + k_n^2) \right] \psi_n F_n = V_{12} \exp ik_1 Z . \psi_1(\mathbf{r}).$$

Multiplying by $\psi_n(\mathbf{r})$, and integrating over all $\mathbf{r}$, we obtain, from the orthogonal property of the wave functions,

$$(\nabla^2 + k_n^2) F_n(\mathbf{R}) = \frac{8\pi^2 m}{h^2} V_n(\mathbf{R}) \exp ik_n Z \quad \ldots\ldots(6),$$

where $$V_n(\mathbf{R}) = \int V_{12}(\mathbf{R}, \mathbf{r}) \psi_0(\mathbf{r}) \psi_n(\mathbf{r}) d\mathbf{r}.$$

From equations (14) and (15) of Chapter II, we see from (6) that the scattered wave F_n is built up from the interference of wavelets scattered by each element of volume, the phase of each wavelet being that of the incident wave, the wave length h/mv_n and of amplitude $\frac{2\pi m}{h^2} V_n dx dy dz/R$. In the case of the wave scattered without change of wave length, V_n is seen to be the potential due to the nucleus, together with that due to static distribution of charge of density $\epsilon | \psi_1(\mathbf{r}) |^2$. The results of Chapter I are correct therefore for elastic scattering. For the inelastic scattering, V_n is the potential due to a charge distribution $\epsilon \psi_1(\mathbf{r}) \psi_n(\mathbf{r})$, and it must be noted that in calculating the interference of the wavelets, account must be taken of their changed wave length. The amplitudes of certain of the inelastically scattered waves have been worked out by Born*.

* *Göttinger Nachrichten*, 1926, p. 146. Born finds that the probability that an electron shall be scattered into a solid angle $d\omega$, after exciting the atom to any one of the states of quantum number 2, is $\cdot 9866 . a^2 v'/v . z_1^{-2} (1 + z_1^2)^{-5}$, where a is the radius of the first Bohr orbit, v, v' the velocities before and after collision, and

$$z_1^2 = \frac{2a}{3} m \sqrt{v^2 + v'^2 - 2vv' \cos\theta}/h.$$

SECTION IV

PAIR OF PARTICLES OF UNEQUAL MASS; THE HYDROGEN ATOM

In Chapter VI, Section II, we found that on the classical theory the equations of motion of a pair of particles, of the same mass, moving in one-dimensional space, were the same as those of a single particle, moving in a plane. We therefore assumed that the wave function describing the pair of particles satisfied the same wave equation as the wave function describing the single particle. The wave equation for a pair of particles of unequal mass can be found by the same method. If m, M, are the masses, then the classical equations of motion are

$$m\ddot{x} = -\frac{\partial V}{\partial x},$$

$$M\ddot{y} = -\frac{\partial V}{\partial y},$$

which are *not* the equations of motion of a particle in a plane. If, however, we express the positions of the two particles by the new coordinates

$$X = x\sqrt{(m/M)},$$
$$Y = y,$$

the equations transform to

$$M\ddot{X} = -\frac{\partial V}{\partial X},$$

$$M\ddot{Y} = -\frac{\partial V}{\partial Y}.$$

These have the required form. We should expect, therefore, that the wave function describing the pair of particles would satisfy the wave equation

$$\frac{ih}{2\pi}\frac{\partial \psi}{\partial t} = \frac{h^2}{8\pi^2 M}\left(\frac{\partial^2 \psi}{\partial X^2} + \frac{\partial^2 \psi}{\partial Y^2}\right) - V\psi.$$

Transforming back to the coordinates x, y, we obtain

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t}=\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi}{\partial x^2}+\frac{h^2}{8\pi^2 M}\frac{\partial^2\psi}{\partial y^2}-V\psi.$$

Analogously, if the two particles have three degrees of freedom each, and masses m_1, m_2, then they will be described by a wave function $\psi(\mathbf{r}_1,\mathbf{r}_2)$ satisfying the wave equation

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t}=\frac{h^2}{8\pi^2 m_1}\nabla_1{}^2\psi+\frac{h^2}{8\pi^2 m_2}\nabla_2{}^2\psi-V\psi \quad \text{.....(7).}$$

As an example, we shall work out the energy levels of the hydrogen atom, treating the nucleus no longer as an abstract centre of force, but as a particle free to move, on the same footing as the electron. Let m_1, m_2 be the masses of the electron and the proton respectively, and $\mathbf{r}_1$, $\mathbf{r}_2$ their coordinates. Our knowledge of the stationary state of the atom, and of the motion of the atom as a whole, will be given by a wave function $\psi(\mathbf{r}_1\mathbf{r}_2)$. The wave function satisfies (7) with V equal to

$$V=-\epsilon^2/|\mathbf{r}_1-\mathbf{r}_2|.$$

The wave equation can be solved by transforming to the coordinates of the centre of mass of the atom, and of the relative position of the electron and proton. We set

$$\mathbf{R}=(m_1\mathbf{r}_1+m_2\mathbf{r}_2)/m_1+m_2),$$
$$\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2.$$

The operator $$\frac{1}{m_1}\nabla_1{}^2+\frac{1}{m_2}\nabla_2{}^2$$

transforms into $$\frac{1}{m}\nabla_r{}^2+\frac{1}{M}\nabla_R{}^2,$$

where $$m=m_1m_2/(m_1+m_2), \qquad M=m_1+m_2.$$

It therefore appears that a solution of (7) is

$$\Psi(\mathbf{R})\,\psi(\mathbf{r}),$$

where Ψ is any solution of

$$\frac{ih}{2\pi}\frac{\partial\Psi}{\partial t}=\frac{h^2}{8\pi^2 M}\nabla^2\Psi \quad \text{.....(8),}$$

and ψ of

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t}=\frac{h^2}{8\pi^2 m}\nabla^2\psi-V\psi \quad \text{.....(9).}$$

Just what solution to take depends on what condition of the atom we want to describe. The equation (8) is the wave equation for a single particle of mass M in free space; therefore our wave function Ψ can give any information about the position and velocity of the centre of mass of the atom that a wave function could give about the position and velocity of a particle of this mass. Ψ, for instance, might represent a wave packet moving in a certain direction. (9), on the other hand, is just the wave equation for a hydrogen atom, and the wave function can vibrate in normal modes, with frequencies ν_1, ν_2, ... given by the Bohr formula

$$h\nu_n = \frac{2\pi m\epsilon^4}{h^2}\,\frac{1}{n^2}.$$

The vibrations, of course, are not in real space, but in the coordinate space of the distance between the electron and the proton. m in formula (9) is, as we have stated, not the mass of the electron, but $m_1 m_2/(m_1 + m_2)$, which is ·05 per cent. smaller. This value of m, rather than m_1, gives agreement with the observed wave lengths of the line spectrum of hydrogen.

SECTION V

SYSTEMS CONTAINING MORE THAN TWO PARTICLES

In this section we shall examine an apparent paradox of the wave mechanics, which arises through our tendency to picture the waves in real space, rather than in the coordinate space of the particles.

The paradox is this: when a beam of de Broglie waves falls on an atom, a wave is scattered, of the same wave length; waves also diverge from the atom, of increased wave length, corresponding to inelastic collisions. Now if de Broglie waves fall on an array of atoms in a crystal, waves are scattered by each atom, both of the same and of increased wave length. The former interfere with each other; the latter do not. Each inelastically scattered wave starts with a definite phase; if we think of the waves as in ordinary space it is difficult to see why they do not interfere.

The waves, however, are not in ordinary space. A system containing a large number of particles, coordinates $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots$ must be described by a wave function of all of them,

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots).$$

For our purpose it will be sufficient to consider a pair of hydrogen atoms, and to show that the waves scattered from them with increased wave length cannot interfere.

Let $\psi_0(\mathbf{r}), \psi_n(\mathbf{r})$ be the wave functions of an atom in its normal and nth stationary states, and with its nucleus at the origin. Let $\mathbf{a}, \mathbf{b}$ be the positions of the nuclei, so that the wave function of an electron, if it is in the atom a, is $\psi(\mathbf{r} - \mathbf{a})$, and if it is in the atom b, $\psi(\mathbf{r} - \mathbf{b})$. We shall suppose the atoms are some distance apart, so that they do not disturb one another. Finally, let $f_a(\mathbf{r}), f_b(\mathbf{r})$ be the amplitudes, at a point $\mathbf{r}$, of the inelastically scattered waves from the atoms $\mathbf{a}, \mathbf{b}$. We have now to find the probability of an electron being found at $\mathbf{r}$, and to see whether it is caused by the interference of the waves, and therefore equal to

$$|f_a(\mathbf{r}) + f_b(\mathbf{r})|^2 \, dx\,dy\,dz,$$

or whether the waves do not interfere, and the probability is

$$[|f_a(\mathbf{r})|^2 + |f_b(\mathbf{r})|^2] \, dx\,dy\,dz.$$

Let $\mathbf{r}_1$ be the coordinate of the colliding electron, and $\mathbf{r}_2, \mathbf{r}_3$ those of the electrons in the two atoms. The wave diverging from the atom at a leaves the atom a excited, and the atom b unexcited; its wave function in the coordinate space is therefore

$$f_a(\mathbf{r}_1)\,\psi_n(\mathbf{r}_2 - \mathbf{a})\,\psi_0(\mathbf{r}_3 - \mathbf{b}).$$

Similarly the wave function of the wave diverging from b is

$$f_b(\mathbf{r}_1)\,\psi_0(\mathbf{r}_2 - \mathbf{a})\,\psi_n(\mathbf{r}_3 - \mathbf{b}).$$

The probability that electron 1 is in the volume element $d\tau_1$, and electrons 2 and 3 in the volume elements $d\tau_2$, $d\tau_3$ respectively, is

$$|f_a(\mathbf{r}_1)\,\psi_n(\mathbf{r}_2 - \mathbf{a})\,\psi_0(\mathbf{r}_3 - \mathbf{b}) + f_b(\mathbf{r}_1)\,\psi_0(\mathbf{r}_2 - \mathbf{a})\,\psi_n(\mathbf{r}_3 - \mathbf{b})|^2 \, d\tau_1 d\tau_2 d\tau_3 \quad \ldots\ldots(10).$$

To obtain the probability that electron 1 is in the volume element $d\tau$, we must integrate (10) over all possible positions of electrons 2 and 3. Owing to the orthogonal properties of the wave functions (Chapter IV, Section IV), we have, *unless* $n = 0$

$$\int \psi_n (\mathbf{r} - \mathbf{a})\, \psi_0 (\mathbf{r} - \mathbf{a})\, d\tau = 0.$$

Therefore, integrating (10) over all $d\tau_2$, $d\tau_3$, we obtain

$$[\, |f_a (\mathbf{r}_1)|^2 + |f_b (\mathbf{r}_1)|^2]\, d\tau_1.$$

The waves, therefore, do not interfere.

If, however, the collision is elastic, (10) reduces to

$$\iiint |\, \psi_0 (\mathbf{r}_2 - \mathbf{a})\, \psi_0 (\mathbf{r}_3 - \mathbf{b})\, |^2 . |\, f_a (\mathbf{r}_1) + f_b (\mathbf{r}_1)\, |^2\, d\tau_1 d\tau_2 d\tau_3,$$

or

$$\int |\, f_a (\mathbf{r}_1) + f_b (\mathbf{r}_2)\, |^2\, d\tau_1.$$

The waves do, therefore, interfere. We may say that two waves can only interfere if the electron that they represent leaves the crystal behind in the same state, whichever wave describes its motion.

Interference would also occur if there was a probability of the same electron exciting both atoms. Waves would then exist having the form

$$f_a (\mathbf{r}_1)\, \psi_n (\mathbf{r}_2)\, \psi_n (\mathbf{r}_3) \qquad \text{.....(11).}$$

If such terms do occur in the complete wave function, then the theory is in contradiction with experiment, for the same electron cannot excite two atoms some distance apart, unless indeed the first atom scatters it towards the second, the probability of which will be very small. A proof that such terms only have very small amplitude can be given by treating the interaction between an atom as a small quantity of the first order, and showing that terms of the form (11) only occur as small quantities of the second order. For this the reader is referred to the original paper*.

* Mott, "Wave Mechanics of α ray Tracks," *Proc. Roy. Soc.* vol. CXXVI, p. 79 (1929).

CHAPTER VIII

THE SPIN OF THE ELECTRON AND THE EXCLUSION PRINCIPLE

SECTION I

It is known from a variety of evidence that many atoms are themselves elementary magnets, possessing both a magnetic moment and a certain moment of momentum. Such atoms, if placed in a magnetic field, will acquire energy due to their magnetic moment. Let us consider what will happen, according to the classical theory, if such an atom were placed in a magnetic field of strength H. Let M be the magnetic moment of the atom, and θ the angle that it makes initially with the field. Then initially the potential energy will be

$$MH \cos \theta \qquad \text{.....(1).}$$

This energy will not remain in the form of potential energy, because the atom will swing about its position of minimum potential energy. (1) will give the total energy of the atom.

Now it is known from experiment that for atoms with one valence electron, the energy of the atom in the field can have only one or other of the values $\pm MH$. The experiment in question is that of Gerlach and Stern. A beam of atoms is sent through an unhomogeneous magnetic field. Let us suppose that the beam moves along the x-axis, and that the field is along the z-axis. Then the beam is split in two in such a way as to show that the force on an atom has one or other of the two values

$$\pm M \frac{\partial H}{\partial z}.$$

We conclude that an atom in a magnetic field can have, due to the field, only one or other of the energies $\pm MH$. This does *not* mean that the direction of the magnetic moment must be either parallel or antiparallel to that of the magnetic field,

because the energy may be partly kinetic, due to the atom swinging about its equilibrium position. The experiment tells us nothing about the direction of the magnetic moment. All we know is that the atom can exist in two "stationary states," one having energy MH, and the other having energy $-MH$.

It is not surprising that we cannot tell the direction in which the magnetic moment points. The electron in a hydrogen atom, we know, can only have energy equal to a certain number of discrete values, and if we know that the atom is in the nth stationary state, then all that we can tell about the position of the electron is, that $|\psi_n(\mathbf{r})|\,dxdydz$ is the probability that it is in the volume element $dxdydz$. In the same way, we should expect that the wave mechanics would provide a description of the behaviour of a magnetic moment in a magnetic field; if we denote the direction of the magnetic moment by a vector $\mathbf{s}$, we should expect the wave mechanics to provide two wave functions, $\chi_I(\mathbf{s})$, $\chi_{II}(\mathbf{s})$, such that if the energy of the atom, due to the magnetic field, is $+MH$, then the probability that the magnetic moment lies in the solid angle $d\omega$ is $|\chi_I(\mathbf{s})|^2 d\omega$. $\chi_{II}(\mathbf{s})$ refers to the energy level $-MH$. What the form of these wave functions is will not concern us in this chapter.

From the Stern-Gerlach experiment, the moment M of atoms with one valence electron is found to be

$$M = \epsilon h/4\pi mc \qquad \ldots\ldots(2).$$

The fact that a *hydrogen* atom has this magnetic moment receives a simple explanation in terms of the Bohr model. For an electron moving with angular momentum I should produce, according to the classical theory*, a magnetic moment M of amount

$$M = \tfrac{1}{2}\epsilon I/mc \qquad \ldots\ldots(3).$$

Now, according to Bohr's theory, we have, for a hydrogen atom in its normal state,

$$I = h/2\pi.$$

* Cf. Andrade, p. 597.

Therefore M has the value given by (2). The Bohr theory, however, fails to explain why the heavier atoms with one valence electron have this angular momentum, for each electron should make a contribution to the total angular momentum; and even if it is only necessary to take the valence electron into account, then we should obtain a magnetic moment that is an integral multiple of (2), because the angular momentum is now an integral multiple of $h/2\pi$. For the silver atom, with which the Stern-Gerlach experiments were originally carried out, the angular momentum of the atom is, according to the Bohr theory, equal to $5h/2\pi$.

The picture of the hydrogen atom provided by the wave mechanics suggests that, in its normal state, the atom will not have any magnetic moment at all. We describe the state of the atom by a wave function

$$\psi = e^{2\pi i\nu t} e^{-r/a}.$$

This wave function is spherically symmetrical; we have shown in Chapter IV that it represents a state of moment of momentum zero. Therefore, by formula (3), the magnetic moment should be zero. A moment of momentum in the direction of the z-axis only appears if k, the magnetic quantum number, is different from zero. The moment of momentum is then $kh/4\pi$, and the magnetic moment

$$\epsilon kh/4\pi mc.$$

The same is true of the wave function that describes the valence electron of any atom with one electron in the outer shell. In the normal state, we have $l = 0$, $k = 0$; the wave function is spherically symmetrical, and there is zero magnetic moment.

We account for the magnetic moment that such atoms undoubtedly possess by the assumption that the electron is itself a little magnet, with magnetic moment $\epsilon h/4\pi mc$, and also with a mechanical moment. This model of the electron has been termed the "spinning" electron, and the moment the "spin" moment. As with the atom, we assume that an electron in a

magnetic field can have energies $\pm MH$, and, as before, we describe the moment of the electron by two wave functions, $\chi_I(\mathbf{s})$ and $\chi_{II}(\mathbf{s})$. If the energy of the electron is $+MH$, then $|\chi_I(\mathbf{s})|^2 d\omega$ is the probability that its spin axis lies in the solid angle $d\omega$ in the direction $\mathbf{s}$.

The ratio of the magnetic moment of an atom to its mechanical moment has been determined directly from the "Gyromagnetic effect*." The ratio is found to be ϵ/mc. Since both the magnetic and the mechanical moment must, according to the wave mechanics, be due to the electron itself and not to its orbital motion, it follows that the mechanical moment of an electron is $h/4\pi$.

We assume then that for a hydrogen atom in its normal state the magnetic moment is due to the "spin" of the electron, and not to the motion of the electron in an orbit. In a heavier atom, each electron will have its characteristic moment, and electrons in states with "magnetic" quantum number k different from zero will have a further moment of amount

$$k \cdot \frac{\epsilon h}{4\pi mc}.$$

Why it is that a completed shell of electrons has zero magnetic moment will be shown later.

SECTION II

THE WAVE FUNCTION FOR A "SPINNING" ELECTRON

Suppose that a hydrogen atom be placed in a strong magnetic field, stronger than any field, due to the motion of the electrons that could exist inside the atom. Let us neglect any effect due to the interaction between the magnetic moment of the electron and the magnetic field caused by the motion of the electron in the field of the nucleus. Then the energy of the electron in the field will have one of the values $\pm MH$, and our knowledge of the direction of the spin axis will be given by one or other of the two wave functions $\chi_I(\mathbf{s})$, $\chi_{II}(\mathbf{s})$. The energy of the electron

* Cf. Andrade, p. 599.

due to its motion will have one of the usual series of values $E_1, E_2, \ldots$, and our knowledge of its position will be given by one of the wave functions $\psi_1(\mathbf{r}), \psi_2(\mathbf{r}), \ldots$. Now, if we have two separate electrons, with wave functions $\psi_a(\mathbf{r})$ and $\psi_b(\mathbf{r})$, and neglect the interaction between them, then the wave function of the pair is the product

$$\psi_a(\mathbf{r}_1)\,\psi_b(\mathbf{r}_2).$$

In the same way, the wave function describing our knowledge of the position of an electron and of its spin will be the product

$$\psi(\mathbf{r})\,\chi(\mathbf{s}).$$

Let us now consider an electron moving in an atom, when there is no external field. Due to its motion through the electrostatic field of the nucleus, there will be a magnetic field, at any moment, acting on the electron. The "spin" magnetic moment of the electron will have a certain energy in this field. Now the time required for the direction of the spin axis to change appreciably, in the field within the atom, is very much greater than the period of the vibrations in the atom.

A proof, depending on this fact, may be given that the atom can exist in two stationary states for every one that would be possible if the electron had no spin. It may further be shown that, if E be the energy of a stationary state without spin, then the energies of the two stationary states *with* spin are $E \pm M\bar{H}_z$, where $\bar{H}_z$ is the value of the magnetic intensity along the z-axis, referred to axes moving with the electron, *averaged* for all possible positions and velocities of the electron. The exact method of this averaging will not be given here.

We describe an electron with energy $E + M\bar{H}_z$ by a wave function $\psi(\mathbf{r})\,\chi_I(\mathbf{s})$, and an electron with energy equal to $E - M\bar{H}_z$ by $\psi(\mathbf{r})\,\chi_{II}(\mathbf{s})$, as before.

The spin therefore causes each energy level to split into two. The lines of hydrogen are in fact observed to consist of doublets, though the theory that we have outlined is too simple to account for them completely, since the relativity change of mass with velocity must also be taken into account.

We see, from considerations of symmetry, that, unless the "magnetic" quantum number k is different from zero, $\bar{H}_z$ will vanish; for if $k = 0$, there is no mean current round the z-axis; the electron is just as likely to be rotating in one direction as in the other.

If the atom is in a stationary state of magnetic quantum number equal to zero, we may still describe it by one or other of the wave functions $\psi(\mathbf{r})\,\chi_I(\mathbf{s})$, $\psi(\mathbf{r})\,\chi_{II}(\mathbf{s})$. Both these wave functions describe a state of the same energy. There is therefore a degeneracy, and so the wave function

$$a_1\psi(\mathbf{r})\,\chi_I(\mathbf{s}) + a_2\psi(\mathbf{r})\,\chi_{II}(\mathbf{s}) \qquad \ldots\ldots(4)$$

describes a stationary state of the same energy. It will be remembered that the two wave functions χ_I and χ_{II} refer to the two possible energies that the electron can have in the magnetic field; it is therefore not surprising that if there is no magnetic field present, the state of the atom can be described by either. The wave function (4) may be given the following interpretation; it describes a state of the atom such that, if a magnetic field were suddenly set up along the z-axis, then the probability that the energy would be MH is $|a_1|^2$, and the probability that it should be $-MH$ is $|a_2|^2$.

It is instructive to consider the order of magnitude of the energy of an electron-magnet in the field of an atom. The magnetic field acting on an electron, moving with velocity v, due to its motion through an electric field of strength F, is of order of magnitude vF/c. The orders of magnitude of v and of F in a hydrogen atom are $2\pi\epsilon^2/h$, $16\pi^4\epsilon^5m^2/h^2$. Therefore the energy of the magnet in the field is of order of magnitude

$$\frac{8\pi^4\epsilon^8 m}{h^4c^2}.$$

This is equal to $\left[\frac{2\pi\epsilon^2}{hc}\right]^2$ times the energy of the atom in its normal state. Now $2\pi\epsilon^2/hc$ is equal to $\frac{1}{137}$; the fineness of the splitting produced by the spin is thus shown.

Now let us suppose that we have two electrons in a helium

atom, and as before that there is some mean magnetic field acting on the electrons, in which the magnetic moments of the electrons could each have energy $\pm MH$. If we neglect the interaction between the two spins, then the energy of the pair of electrons will have one or other of the three values

$$+ 2MH, \quad 0, \quad - 2MH.$$

We should expect, therefore, that each stationary state of the helium atom would be observed, on close resolution, to consist of three.

It is actually found that the states of parhelium are triplets, and the states of orthohelium singlets. To see why this is, we must consider the interaction between the moments of the two electrons.

First, neglecting the spin, let the wave function of the helium atom in its nth stationary state be $\psi_n(\mathbf{r}_1\mathbf{r}_2)$. Then, if we neglect the influence of the spin on the orbital motion of the electrons, it is clear that the wave function of the atom with spin must be of the form

$$\psi_n(\mathbf{r}_1\mathbf{r}_2)\,\chi(\mathbf{s}_1\mathbf{s}_2) \qquad \ldots\ldots(5),$$

where χ is some unknown wave function, and $\mathbf{s}_1$, $\mathbf{s}_2$ define the directions of the spin axes of the two electrons. Our problem is to find how many normal modes the wave function $\chi(\mathbf{s}_1\mathbf{s}_2)$ is capable of, if we take into account the interaction between the spin magnetic moments; and to find out why it is that for orthohelium χ appears to have three normal modes, and for parhelium only one.

Consider first two electrons at rest in a magnetic field. Neglect first of all the interaction between the spin moments; then our knowledge of the direction of the spin magnetic moment is specified by a wave function $\chi_\alpha(\mathbf{s})$, where the suffix α denotes either I or II according as the energy of the magnet is $\pm MH$. Our knowledge of the pair of spin axes will be specified by the wave function

$$\chi_\alpha(\mathbf{s}_1)\,\chi_\beta(\mathbf{s}_2) \qquad \ldots\ldots(6),$$

where both α and β may denote either I or II. The energy of the pair may have either of the three values

$$+2MH, \quad 0, \quad -2MH,$$

which are represented on the left of Fig. 19. The energy value zero is degenerate, since the two wave functions $\chi_I(\mathbf{s}_1)\,\chi_{II}(\mathbf{s}_2)$ and $\chi_I(\mathbf{s}_2)\,\chi_{II}(\mathbf{s}_1)$ both describe a system with that energy.

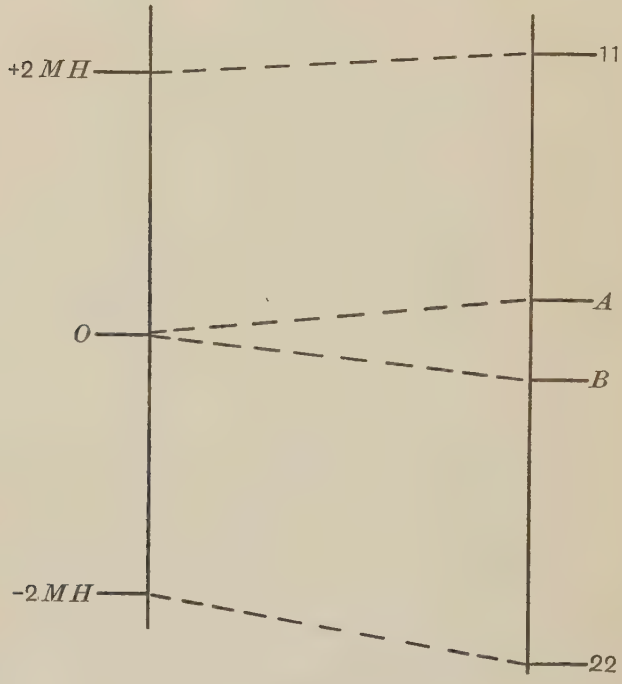


Fig. 19.

Now let us suppose that there is a small interaction between the magnetic moments of the two electrons; then we have a phenomenon similar to that considered in Chapter VI, Sections II and III. The wave function (6), so long as α and β are different, does not represent a first approximation to the true normal

mode of the system; the true normal modes are, to a first approximation,

$$\chi_\alpha(\mathbf{s}_1)\,\chi_\beta(\mathbf{s}_2) \pm \chi_\alpha(\mathbf{s}_2)\,\chi_\beta(\mathbf{s}_1),$$

and these two normal modes have slightly different frequencies. Now α and β are each capable of only two values; so the system is capable of the four normal modes

$$\left.\begin{aligned}
\chi_{11}(\mathbf{s}_1\mathbf{s}_2) &= \chi_I(\mathbf{s}_1)\,\chi_I(\mathbf{s}_2)\\
\chi_A(\mathbf{s}_1\mathbf{s}_2) &= \chi_I(\mathbf{s}_1)\,\chi_{II}(\mathbf{s}_2) - \chi_I(\mathbf{s}_2)\,\chi_{II}(\mathbf{s}_1)\\
\chi_B(\mathbf{s}_1\mathbf{s}_2) &= \chi_I(\mathbf{s}_1)\,\chi_{II}(\mathbf{s}_2) + \chi_I(\mathbf{s}_2)\,\chi_{II}(\mathbf{s}_1)\\
\chi_{22}(\mathbf{s}_1\mathbf{s}_2) &= \chi_{II}(\mathbf{s}_1)\,\chi_{II}(\mathbf{s}_2)
\end{aligned}\right\} \quad \ldots\ldots(7).$$

The way in which the energy levels of these four normal modes arise from the original energy levels, when the interaction is introduced, is shown in Fig. 19.

It will be noticed that all four wave functions, except χ_A, are "symmetrical" in $\mathbf{s}_1, \mathbf{s}_2$. χ_A is antisymmetrical.

Now suppose that the electrons are brought nearer together, so that the interaction between the spin magnets becomes larger and larger; then the interval between the energy levels I and II becomes larger and larger. Then (7) will no longer be a good approximation to the wave functions. But we shall still have a wave function $\chi(\mathbf{s}_1\mathbf{s}_2)$ describing our knowledge of the spins, and χ will be capable of vibrating in four normal modes, of which three will be symmetrical in $\mathbf{s}_1\mathbf{s}_2$, and one antisymmetrical. This will still be the case, even if there is no magnetic field acting on the spins, except that arising from their own interaction.

Now let us consider once again two electrons in a helium atom. The interaction between the spins is of the order of magnitude M^2/R^3, where R is the mean distance between the electrons. This is easily seen to be of the same order of magnitude as the energy of one of them, in the magnetic field due to its motion in the field of the nucleus.

The electrons in a helium atom are by no means at rest, so the interaction between their spin moments is not constant.

Without further investigation, therefore, it is not clear that the effect of the interaction between the spins will be, as before, to enable $\chi(\mathbf{s}_1\mathbf{s}_2)$ to vibrate in four separate normal modes with different energies. To show this, it is necessary to take the wave function for two electrons with spin, and to show that the first approximation to the solution has the form (5), and that $\chi(\mathbf{s}_1\mathbf{s}_2)$ has these four stationary states. This has been done by Gaunt*, who used the equation of Dirac for an electron with spin. We shall simply assume that the two spins may be treated as though the electrons were at rest in the atom.

It follows that the helium atom in its nth normal state may be described by a wave function

$$\psi_n(\mathbf{r}_1\mathbf{r}_2)\,\chi(\mathbf{s}_1\mathbf{s}_2),$$

where χ can vibrate in four separate normal modes with different energies. It seems, therefore, that each energy level of the atom without spin should under close resolution split up into four. We have to enquire why it is that in orthohelium only three of these four possible lines are ever observed, and in parhelium only one.

In Chapter VI it was shown that if two electrons, coordinate $\mathbf{r}_1, \mathbf{r}_2$, are absolutely identical, and have no spin, then it is impossible for them to pass from a state that is symmetrical in $\mathbf{r}_1, \mathbf{r}_2$ to a state that is antisymmetrical. The proof depended on the fact that if $V(\mathbf{r}_1, \mathbf{r}_2)$ is the potential of the two electrons in any field whatever, then V is unaltered if we interchange the position of the two electrons; from which fact we deduce that

$$V(\mathbf{r}_1, \mathbf{r}_2) = V(\mathbf{r}_2, \mathbf{r}_1) \qquad \ldots\ldots(8).$$

Now (8) is not strictly true for real electrons, because the potential energy will depend also on the spin. It is, however, accurately true that, if $V(\mathbf{r}_1\mathbf{s}_1; \mathbf{r}_2\mathbf{s}_2)$ is the potential energy of the pair of electrons in any field, then

$$V(\mathbf{r}_1\mathbf{s}_1; \mathbf{r}_2\mathbf{s}_2) = V(\mathbf{r}_2\mathbf{s}_2; \mathbf{r}_1\mathbf{s}_1).$$

* Gaunt, *Proc. Roy. Soc.* vol. CXXII (1929).

From this fact we can deduce, by the method of Chapter VI, that if the electrons are in a state described by a wave function such that

$$\psi(\mathbf{r}_1\mathbf{s}_1;\mathbf{r}_2\mathbf{s}_2) = -\psi(\mathbf{r}_2\mathbf{s}_2;\mathbf{r}_1\mathbf{s}_1),$$

then it cannot get into a state described by a wave function such that

$$\psi(\mathbf{r}_1\mathbf{s}_1;\mathbf{r}_2\mathbf{s}_2) = +\psi(\mathbf{r}_2\mathbf{s}_2;\mathbf{r}_1\mathbf{s}_1).$$

The first type of wave function we shall call "antisymmetrical in the electrons," by which we mean that if we interchange the whole group of coordinates ($\mathbf{r}$, $\mathbf{s}$) that describes an electron, we change the sign of the wave function. The second type we call "symmetrical in the electrons."

Now let us consider an energy level of parhelium. The wave function $\psi(\mathbf{r}_1\mathbf{r}_2)$ is symmetrical in $\mathbf{r}_1\mathbf{r}_2$. The energy level should, on account of the spin, split up into four components. The wave functions of three of these are symmetrical in the spins $\mathbf{s}_1$, $\mathbf{s}_2$, the other is antisymmetrical. Three, therefore, of the complete wave functions (5) are "symmetrical in the electrons," and one is antisymmetrical. *It is only the latter that ever appears in nature.* The lines of parhelium are therefore singlets.

Consider now an energy level of orthohelium; the wave function $\psi(\mathbf{r}_1\mathbf{r}_2)$ is antisymmetrical in $\mathbf{r}_1\mathbf{r}_2$. Therefore, of the complete wave functions (5), one is symmetrical and three are antisymmetrical. Again, it is only the energy levels having antisymmetrical wave functions that are found in nature. On account of the spin, therefore, the lines of orthohelium are split into triplets.

To account for the singlets and triplets of helium, then, we have to enunciate a new law. Out of the energy levels predicted by the wave mechanics as possible, only those are ever found in nature for which the wave function is antisymmetrical in the coordinates (including $\mathbf{s}$) of the two electrons. The law is consistent, because, as we have shown, there are no transitions predicted by the wave mechanics between "symmetrical" states and "antisymmetrical" states. Thus, if a helium atom is initially in an allowed state (antisymmetrical), the wave mechanics pre-

dict that it will remain in an allowed state. Why it is that all atoms begin in antisymmetrical states is not at present known.

In conclusion, it must be stated that the phenomenon of the spin has been shown by Dirac* to be a consequence of the application of the theory of relativity to the wave mechanics. An electron, so to speak, cannot obey the restricted principle of relativity, and at the same time be describable by a wave function, unless it has a spin magnetic moment.

SECTION III

THE EXCLUSION PRINCIPLE

It was known before the discovery of the wave mechanics that, in an atom, no two electrons could be in the same quantum state. In other words, no two electrons can have the same set of quantum numbers. To this fact is ascribed the existence of successive rings in the atom, the K ring with two electrons, the L ring with eight, the N ring with eighteen, the M ring with thirty-two. The principle was first enunciated by Pauli, and is known as the exclusion principle.

We shall show that the law that we assumed in the last section, that stationary states are only found whose wave functions are antisymmetrical in the electrons, is, when generalised to the case of many electrons, equivalent to the exclusion principle enunciated above.

Let θ denote the group of coordinates $(\mathbf{r}, \mathbf{s})$ that describe the position of an electron and the direction of the spin axis. Then an atom with N electrons will be described by a wave function

$$\psi(\theta_1, \theta_2, \ldots \theta_N).$$

The field in which each electron moves is due both to the nucleus and to the other electrons. Let us, to a first approximation, suppose that the electrons move in a spherically symmetrical field $V(r)$, which may be found by the method of Hartree described in the last chapter. $\frac{\partial V}{\partial r}$ will be equal to

* Dirac, *Proc. Roy. Soc.* vol. CXVII, p. 610.

$N\epsilon^2/r^2$ near the nucleus, and will tend to ϵ^2/r^2 for large r. Let us neglect each part of the interaction between the electrons as is not included in $V(r)$. Then each electron will have its wave function $\psi_a(\theta)$, $\psi_b(\theta)$, ..., and its energy E_a, E_b, ... The energy of the whole atom will be

$$E_a + E_b + \ldots + E_N \qquad \ldots\ldots(9),$$

and the wave function

$$\psi_a(\theta_1)\,\psi_b(\theta_2)\ldots \qquad \ldots\ldots(10.1).$$

The wave function is degenerate, for, if p, q, r, ... is any permutation of the first N integers, then the wave function

$$\psi_a(\theta_p)\,\psi_b(\theta_q)\ldots \qquad \ldots\ldots(10.2)$$

describes an atom with the same energy. There are in fact $N!$ different wave functions, all with the same energy. Further, any linear combination of these will describe the atom.

The determinant

$$\begin{vmatrix} \psi_a(\theta_1) & \psi_a(\theta_2)\ldots \\ \psi_b(\theta_1) & \psi_b(\theta_2)\ldots \\ \ldots\ldots\ldots\ldots\ldots\ldots \end{vmatrix} \qquad \ldots\ldots(10.3)$$

is a linear combination of some of these $N!$ wave functions. It is easily seen that it is antisymmetrical in *any* pair of electrons, for if we interchange any two columns of a determinant we change its sign. The determinant vanishes if any two columns are the same; therefore, if any two electrons are in the same state, the atom cannot be described by an antisymmetrical wave function.

Consider now the *exact* wave function $\psi(\theta_1\theta_2\ldots\theta_N)$ of the atom, in which the interaction between the electrons is not neglected. Let us make the assumption that only those stationary states are found in nature for which the wave function is antisymmetrical in *each* pair of electrons.

As much of the interaction energy as possible being included in the field $V(r)$, the true energies of the atom will not differ very much from (9). Since the wave function must be antisymmetrical, only those energy levels (9) will occur for which an antisymmetrical wave function of the form (10.3) can be found, which does not vanish. It follows that of the suffixes

$a, b, c, \ldots$ in (9), no two must refer to the same quantum state. Therefore no two electrons can be in the same quantum state.

We now enquire how many electrons can be in the K ring. An electron in the K ring has principal quantum number n equal to unity; we saw in Chapter IV that this implies that the other two quantum numbers, l and k, should both vanish. The spin quantum number, that we have designated by α, can have two values, according as the energy of the electron-magnet has the value $\pm MH$. If therefore $n = 1$, there are two possible values of the group of numbers (l, k, α). Therefore no more than two electrons can occupy the K ring.

In the L ring, n is equal to two. We can therefore have

$$\begin{aligned} l &= 1, \qquad k = -1, 0, +1. \\ l &= 0, \qquad k = \quad 0. \end{aligned}$$

α as before has two values. The group $(lk\alpha)$ has therefore eight values. Thus eight electrons fill the L ring.

In the M ring, with $n = 3$, we have

$$\begin{aligned} l &= 2, \qquad k = -2, -1, 0, 1, 2. \\ l &= 1, \qquad k = \quad -1, 0, 1. \\ l &= 0, \qquad k = \quad\quad 0. \end{aligned}$$

The total number of states is therefore

$$2 \times (5 + 3 + 1) = 18.$$

In the N ring, the total number is similarly

$$2 \times (7 + 5 + 3 + 1) = 32.$$

The next ring could accommodate fifty electrons, but as the series of elements stops short at uranium, with atomic number ninety-two, this group is never filled.

As we remarked before, a completed ring has zero magnetic moment. It is seen that, if M is the spin moment, then for every electron with energy $+ MH$ in an external magnetic field, there is an electron with energy $- MH$. Therefore the spins will

not contribute anything to the magnetic moment. Further, an electron in a state of magnetic quantum k has magnetic moment $\epsilon kh/4\pi mc$, either parallel or antiparallel to the z-axis, according to the sign of k. Now, to every electron with magnetic quantum number k, there is an electron in the shell with magnetic quantum number $-k$. Thus the completed shell has zero magnetic moment.

SECTION IV

SPECIFIC HEAT OF THE FREE ELECTRONS IN A METAL

It was a well-known difficulty of the electron theory of metals that if the number of free electrons was of the same order of magnitude as the number of atoms in the metal, then the heat energy of the electrons would be of the same order of magnitude as the heat energy of the atoms, and the electrons would make a very considerable contribution to the specific heat. This is not in agreement with experiment; the Debye theory accounts very well for the specific heats of solids*, without taking account of the electrons at all.

Now, it was shown in Chapter IV that an electron shut up in a box could not have any energy, but could only exist in stationary states of energy

$$\frac{h^2}{8m}\left(\frac{n_1^2 + n_2^2 + n_3^2}{a^2}\right) \qquad \text{.....(11).}$$

a is the length of the box, supposed square, n_1, n_2, n_3 are integers. The electrons in a metal behave as "electrons in a box," and so can only exist in stationary states with these energies. We neglect the effect of the field due to the atoms. Now, by the exclusion principle, no two electrons can be in the same state. Corresponding to each set of values of the quantum numbers n_1, n_2, n_3, there will be two stationary states; one for each value of the spin quantum number α. Therefore, even if the metal be

* Cf. Jeans, *Dynamical Theory of Gases*, Chap. XVII.

at the absolute zero of temperature, only two electrons can have zero energy. Six electrons can have energy $h^2/8ma^2$; six can have energy $2h^2/8ma^2$; and so on. We see then that even at absolute zero the energy of the electrons does not disappear.

The order of magnitude of the average energy of an electron in a metal is thus found to be 2 or 3 volts. It is therefore only at high temperatures that an appreciable number of the electrons will

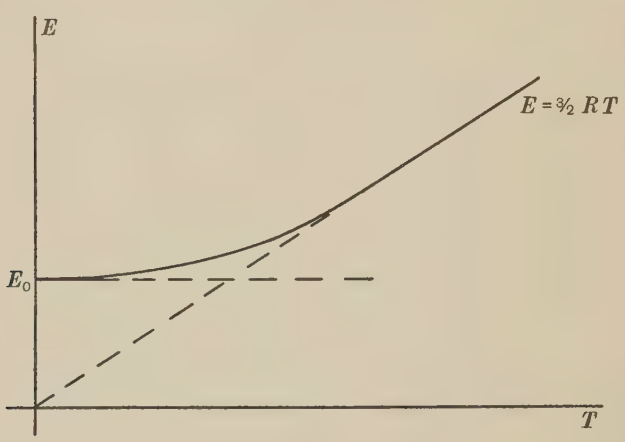


Fig. 20.

have energy greater than at absolute zero. The average energy E of an electron, plotted against T, is shown in Fig. 20. At low temperatures (including ordinary room temperatures) the energy is nearly constant. At high temperatures, at which $\frac{3}{2}RT$ is equal to two or three electron volts, E tends to the classical value $\frac{3}{2}RT$. Since at ordinary temperatures the slope of the curve is very much smaller than at high temperatures, the specific heat $\frac{dE}{dT}$ is very much less than the classical value $\frac{3}{2}R$. This difficulty in the electron theory of metals is therefore removed by the wave mechanics*.

* For a fuller discussion see Sommerfeld, *Z. Physik*, vol. XLVII, p. 1 (1928).

APPENDIX

NOTE 1

According to the theory of relativity, the energy W of a moving particle is

$$m_0 c^2 \left(1 - \frac{v^2}{c^2}\right)^{-\frac{1}{2}}.$$

The momentum p is

$$m_0 v \Big/ \sqrt{1 - \frac{v^2}{c^2}}.$$

The energy therefore can be expressed in terms of the momentum

$$W = c\sqrt{(m_0{}^2 c^2 + p^2)}.$$

If the rest mass be zero, therefore,

$$W = cp.$$

NOTE 2

Proof of F Formula

Let O be the centre of the scattering medium.

Let us consider the waves scattered through an angle θ. Let Ox make an angle $\frac{1}{2}\theta$ with the direction of incidence of the light. Then the wavelets scattered from any plane parallel to Ox will all be in phase, and the wavelets scattered from two planes distant y from each other will have a phase difference μy, where $\mu = 4\pi \sin \frac{1}{2}\theta/\lambda$. The resultant, therefore, of all the scattered wavelets will have amplitude, at a large distance R from O, of

$$\frac{1}{R} \iiint e^{i\mu y} P(r)\, dx dy dz.$$

Expressing this in spherical polar coordinates, we have

$$\frac{1}{R}\, 2\pi \int_0^\infty \int_0^\pi e^{i\mu r \cos\theta} P(r)\, r^2\, dr \sin\theta d\theta.$$

Carrying out the θ integration, we obtain

$$\frac{1}{R}\,4\pi\int_0^\infty \frac{\sin\mu r}{\mu r}\,P\,(r).r^2dr.$$

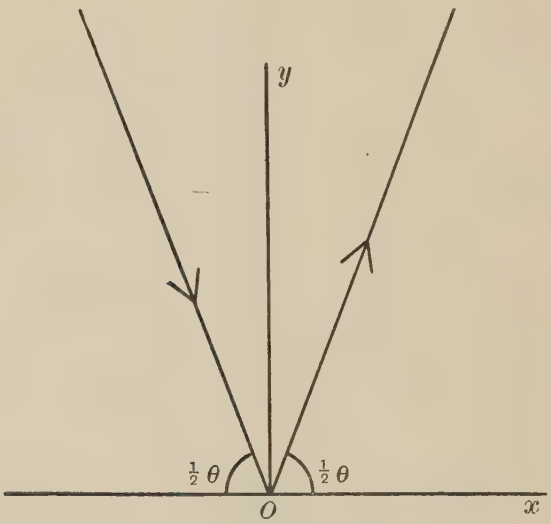


Fig. 21.

NOTE 3

We have

$$f\,(\theta) = \frac{8\pi^2 m}{h^2}\int_0^\infty \frac{\sin\mu r}{\mu r}\,V\,(r)\,r^2dr \qquad \ldots\ldots(1),$$

where $$\nabla^2 V = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial V}{\partial r}\right) = 4\pi\rho \text{ and } V \sim \frac{Z}{r}$$

at the origin.

A single partial integration of (1) leads to

$$f\,(\theta) = \frac{8\pi^2 m}{h^2}\int_0^\infty \left[\frac{r\cos\mu r}{\mu^2} - \frac{\sin\mu r}{\mu^3}\right]\frac{\partial V}{\partial r}\,dr.$$

A second partial integration leads to

$$\frac{8\pi^2 m}{h^2}\left[\frac{r\sin\mu r}{\mu^3}\frac{\partial V}{\partial r}\right]_0^\infty - \frac{8\pi^2 m}{h^2}\int_0^\infty \frac{\sin\mu r}{\mu^3 r}\,4\pi\rho\,(r)\,r^2 dr,$$

which reduces to $$\frac{8\pi^2 m}{h^2}\,[Z - F]/\mu^2,$$

which is equivalent to (9).

NOTE 4

It is required to prove that, if ψ satisfies the wave equation

$$\frac{ih}{2\pi}\frac{\partial\psi}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2\psi - V\psi \qquad \text{.....(1),}$$

and tends to zero exponentially for large r, then

$$\frac{\partial}{\partial t}\iiint \psi\psi^X dx\,dy\,dz = 0,$$

where ψ^X is the complex conjugate of ψ.

Taking the complex conjugate of (1), we have

$$-\frac{ih}{2\pi}\frac{\partial\psi^X}{\partial t} = \frac{h^2}{8\pi^2 m}\nabla^2\psi^X - V\psi^X \qquad \text{.....(2).}$$

Multiplying (1) by ψ^X and (2) by ψ, and subtracting one from the other, we obtain

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}[\psi\psi^X] = \frac{h^2}{8\pi^2 m}(\psi^X\nabla^2\psi - \psi\nabla^2\psi^X).$$

If we integrate both sides of this equation over any volume W, we have by Green's theorem that

$$\frac{ih}{2\pi}\frac{\partial}{\partial t}\iiint_W \psi\psi^X\,dx\,dy\,dz = \frac{h^2}{8\pi^2 m}\iint\left[\psi^X\frac{\partial\psi}{\partial n} - \psi\frac{\partial\psi^X}{\partial n}\right]dS,$$

the surface integral being taken over the surface of W. As we take W larger and larger, the surface integral tends to zero. Therefore, if the integral is taken over all space,

$$\frac{\partial}{\partial t}\iiint \psi\psi^X dx\,dy\,dz = 0.$$

NOTE 5

Let $\psi_n(r)$, $\psi_l(r)$ be the wave functions for a single electron in a field $V(r)$. The two functions satisfy the wave equations

$$\nabla^2\psi_n + \frac{8\pi^2 m}{h^2}(E_n - V(r))\psi_n = 0,$$

$$\nabla^2\psi_l + \frac{8\pi^2 m}{h^2}(E_l - V(r))\psi_l = 0.$$

If two electrons move in the field $V(r)$, and if the interaction is neglected, the wave function that describes them satisfies the equation

$$(\nabla_1^2 + \nabla_2^2)\psi + \frac{8\pi^2 m}{h^2}(E - V(r_1) - V(r_2))\psi = 0 \quad \ldots\ldots(1).$$

The values of E for which a solution can be found that falls off exponentially for large r_1, r_2, are clearly

$$E = E_n + E_l,$$

and the most general solution of (1) corresponding to this value of E is

$$\psi^0 = a\psi_n(r_1)\psi_l(r_2) + b\psi_n(r_2)\psi_l(r_1) \quad \ldots\ldots(2),$$

where a and b are arbitrary constants.

Suppose now that there is a *small* interaction energy $U(r_1, r_2)$ between the electrons, so that the wave equation is

$$(\nabla_1^2 + \nabla_2^2)\psi + \frac{8\pi^2 m}{h^2}(E_l + E_m + \epsilon - V(r_1) - V(r_2) - U(r_1 r_2))\psi = 0 \ldots\ldots(3).$$

ϵ is the displacement of the energy level of the system, due to the interaction energy U. The solutions of the equation will then be of the form

$$\psi^0 + f \quad \ldots\ldots(4),$$

where f is small. We expand f as a series

$$f = \sum_{l'}\sum_{n'} C_{n'l'}\psi_{n'}(r_1)\psi_{l'}(r_2).$$

If we substitute (4) into (3), and neglect the small products Uf, ϵf, we obtain

$$\sum_{n'l'}\sum [E_n + E_l - E_{n'} - E_{l'}]\, C_{n'l'}\, \psi_{n'}(r_1)\, \psi_{l'}(r_2) = -[\epsilon - U(r_1 r_2)]\, \psi^0 \qquad \ldots\ldots(5).$$

Now multiply (5) by $\psi_n{}^X(r_1)\, \psi_l{}^X(r_2)$ and integrate over all r_1, r_2. Owing to the orthogonal property of the wave functions, the left-hand side of this equation vanishes; if then we set

$$K = \iint U(r_1 r_2) \mid \psi_n(r_1) \mid^2 \mid \psi_l(r_2) \mid^2 dr_1 dr_2,$$

$$S = \iint U(r_1 r_2)\, \psi_n{}^X(r_1)\, \psi_n(r_2)\, \psi_l{}^X(r_1)\, \psi_l(r_2)\, dr_1 dr_2,$$

the equation reduces to

$$(\epsilon - K)\, a - bS = 0.$$

If we multiply (5) by $\psi_n(r_2)\, \psi_l(r_1)$ and integrate over all r_1, r_2, we obtain

$$-aS + (\epsilon - K)\, b = 0.$$

Eliminating a, b, we have

$$(\epsilon - S)^2 = K^2,$$

and therefore

$$\epsilon = S \pm K.$$

It follows that ϵ can have two values. Thus, for every energy level of the unperturbed system, there are two for the system with interaction.

If $\epsilon = S - K$ then a is equal to $+ b$, and the wave function is symmetrical. If $\epsilon = S + K$, then a is equal to $- b$, and the wave function is antisymmetrical.

INDEX

Aether, 2
α particles, disintegration of, 77
  scattering of, 23, 34
  statistics, 118
Azimuthal quantum number, 76

Bohr atom, 56
Born, 129
de Broglie waves, 8

Conservation of energy, 69
Compton effect, 5, 90

Davisson and Germer, 7
Degeneracy, 71
Dirac, 90, 146

Elliptic orbits, 76

Gamow, 77
Gaunt, 144
Geiger-Nuttall law, 81
Gerlach and Stern, 135
Group velocity, 40
Gyromagnetic effect, 138

Hartree, 120
Heisenberg, 110
Heitler, 112
Helium atom, 109
Helium molecule, 117
Hydrogen atom, 63, 71, 130
Hydrogen molecule, 110
Hydrogen molecular ion, 94

Interference, 2

K ring, 148

L ring, 148

Light quanta, 4, 5
London, 112

Magnetic moment of atom, 135
Magnetic quantum number, 77
Membrane, 104
Mott, 134

Non-combining terms, 113

Orthogonal property, 65

P electrons, 77
Photoelectric effect, 4
Potential jump, 15

Reflection of waves, 35
Refraction of waves, 10
Rutherford scattering law, 24, 34

Scattering of α particles, 23
  of electrons, 20, 33, 125
  of X-rays, 25
Schrödinger's equation, 33
Self-consistent field, 119
S electrons, 77
Sommerfeld, 150
Specific heat of electrons in metal, 149
Stationary states, 56

Uncertainty relation, 47

Waller, 90
Wave equation, 33, 43
Wave function, 16
Wave length, 7
Wave packet, 39

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